HETEROGENEOUS EQUILIBRIA BETWEEN AQUEOUS AND METALLIC SOLUTIONS

THE INTERACTION OF MIXED SALT SOLUTIONS AND LIQUID AMALGAMS

A STUDY OF THE IONIZATION RELATIONS OF POTASSIUM AND STRONTIUM CHLORIDES IN MIXTURES

BY

EDWIN ARTHUR REES

A.B. University of Denver, 1913
A.M. University of Denver, 1914

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

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1918

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I wish to express my thanks for the help of Dr. G. McP. Smith, under whose direction this investigation was carried out. Association with him during the last four years has always been a source of inspiration and has made the study a real enjoyment.

Edwin A. Rees.

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HETEROGENEOUS EQUILIBRIA BETWEEN AQUEOUS AND METALLIC SOLUTIONS: THE INTERACTION OF MIXED SALT SOLUTIONS AND LIQUID AMALGAMS.

A STUDY OF THE IONIZATION RELATIONS OF POTASSIUM AND STRONTIUM CHLORIDES IN MIXTURES.

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A. Introduction.

1. Purpose of the Investigation.—This investigation is the fifth of a series undertaken in this laboratory with the object of studying the ionic relationships which exist in aqueous solutions of mixed strong electrolytes, particularly in the region of "concentrated" solutions. The present work comprises a study of the mixed chlorides of potassium and strontium at total concentrations ranging from 0.05 N to 3.00 N. The method employed is based upon a distribution equilibrium of the two molecular species, potassium and strontium, between two non-miscible phases, water and mercury, as originally developed by G. McP. Smith.[1]

2. Principles Relating to the Ionization of Salts.—Van't Hoff[2] has shown that the colligative properties of dilute solutions are intimately connected by a set of relations which must of necessity follow from the

[1] G. McP. Smith, *Am. Chem. J.*, **37**, 506 (1907); *J. Am. Chem. Soc.*, **32**, 502 (1910); **35**, 39 (1913); G. McP. Smith and T. R. Ball, *Ibid.*, **39**, 179 (1917); G. McP. Smith and S. A. Braley, *Ibid.*, **39**, 1545 (1917); **40**, 197 (1918).

[2] J. H. van't Hoff, *Z. physik. Chem.*, **1**, 481 (1887).

two laws of thermodynamics. These relations may now in general be applied to all solutions of constant thermodynamic environment.[1] The failure of the application of these principles to the more general class of solutions, those of variable thermodynamic environment, may be attributed to the occurrence of complex chemical processes between the different molecular species in the solution, the nature and extent of which are often by no means well known.

The anomalous behavior of van't Hoff's generalizations, when applied to aqueous solutions of variable thermodynamic environment which conduct electricity, led Arrhenius[2] to propose the ionic theory. Any successful interpretation of the behavior of solutions of electrolytes can now be made only in the light of this theory, and such an interpretation necessarily involves *a knowledge of the different ionic species present,* as well as of their individual concentrations.

Even with solutions as dilute as 0.1 N, there is no strict agreement in the degrees of ionization found by the different methods available, namely the methods involving colligative properties and the Arrhenius conductivity method. Nevertheless, the conductance ratio Λ/Λ_0, Λ corrected if necessary for viscosity, has been considered the reliable method of measuring the degree of ionization of at least uni-univalent electrolytes, but only in dilute solutions.

The conductivity study has been extended to mixtures of salts, and data are available, in the work of Arrhenius,[3] Barmwater,[4] MacGregor, Archibald, McIntosh and McKay,[5] Sherrill,[6] and Sandonnini,[7] for every possible combination of uni-univalent, uni-bivalent, bi-univalent and bi-bivalent types. Mixtures of salts with no common ion, with a common anion and with a common cation have been studied, and Barmwater has even extended the study to mixtures of 3 and 4 electrolytes. And in all cases, with only slight deviations, it has been found that the measured specific conductance of a mixture agrees fairly well with the specific conductance as calculated additively from the measured specific conductances of the separate salts, assuming that the ratio of the partial conductances of the salts in the mixture is the same as that of the specific conductances of separate solutions containing the electrolytes at equivalent concentrations equal to those which exist in the mixture. Solutions of this type were called isohydric by Arrhenius.

[1] E. W. Washburn, "Principles of Physical Chemistry," pp. 142, 220; *J. Am. Chem. Soc.*, **32**, 653 (1910).

[2] Svannte Arrhenius, *Z. physik. Chem.*, **1**, 631 (1887).

[3] Svannte Arrhenius, *Ibid.*, **2**, 284 (1888).

[4] F. Barnwater, *Ibid.*, **28**, 427 (1899).

[5] *Trans. Nova Scotia Inst. Sci.*, **9** and **10** (1895–1899).

[6] M. S. Sherrill, *J. Am. Chem. Soc.*, **32**, 741 (1910).

[7] C. Sandonnini, *Atti. Inst. Veneto*, **74**, 519 (1915); *Gazz. chim. ital.*, [2] **46**, 205 (1916).

In the case of uni-univalent electrolytes, with which conductivity is generally regarded as a measure of ionization, the isohydric principle would require that the degree of ionization of either of the two electrolytes in a binary common-ion mixture should be identical with that which it has in its own pure solution in which its positive or negative ions have a concentration equal to that of the common ion in the mixture. In equivalent mixtures of sodium and potassium chloride, for example, if conductivity is really a measure of ionization, and if the isohydric principle holds, the data would indicate that the ion fraction of potassium is somewhat greater than that of sodium. Smith and Ball,[1] however, have studied sodium and potassium chloride solutions, mixed in equivalent proportions, by means of the distribution method between water and mercury and found that the ion fraction of sodium gains upon that of potassium as the concentration is increased.

Transference experiments have been carried out by McKay[2] with mixed solutions containing potassium chloride and sulfate, 0.2009 *N* with respect to each salt. Upon the assumption that the transference number of the chlorine of the potassium chloride in this mixture is the same (0.504) as in dilute solutions of potassium chloride, the proportion of the current carried by the ions of this salt was found to be 0.573 and the proportion carried by the ions of the potassium sulfate 0.427. By multiplying these values by the measured specific conductance of the mixture, the partial specific conductance of the potassium chloride was found to be 2% larger, and that of the potassium sulfate 5.2% smaller than the value calculated on the basis of the isohydric principle. But, nevertheless, though the ratio of the actual partial conductances of the two salts is 7.5% larger than that required by the principle, the observed conductance of the mixture was found to differ from the sum of the calculated partial conductances by only about one %.

More recently, Loomis and Meacham[3] have shown that, within the limits of our knowledge of the contact potential of the system

$$0.1\ N\ \mathrm{HCl} - 0.1\ N\ \mathrm{KCl},$$

the potential of the 0.1 *N* hydrochloric acid calomel electrode is identical with that of the 0.1 *N* potassium chloride calomel electrode, thereby indicating that at 0.1 *N* concentration hydrochloric acid and potassium chloride have approximately equal degrees of ionization. In the case of these uni-univalent ionogens, the isohydric principle has been tested by Loomis, Essex and Meacham[4] (with the use of the apparatus and method

[1] *Loc. cit.*

[2] G. M. J. McKay, *J. Am. Chem. Soc.*, **33**, 308 (1911).

[3] N. E. Loomis and M. R. Meacham, *Ibid.*, **38**, 2310 (1916).

[4] N. E. Loomis, J. L. Essex and M. R. Meacham, *Ibid.*, **39**, 1133 (1917).

of Loomis and Meacham) by means of electromotive-force measurements on the system

$$H_2 — Pt — 0.1\ N\ (HCl + KCl) — Hg_2Cl_2 — Hg,$$

for mixtures ranging from (0.09 N HCl + 0.01 N KCl) to (0.01 N HCl + 0.09 N KCl). In every case the electromotive force was found to be higher than the value calculated with the use of the isohydric principle, on the assumption of a constant chloride-ion concentration in these mixtures. The authors conclude that the isohydric principle does not apply rigidly (even in this simple case, at 0.1 N concentration), but that there is a slight increase in the ionization of the hydrochloric acid as its fraction in the mixture decreases.

For solutions of even single salts of the uni-bivalent type, there is no satisfactory method for the determination of ion concentrations. Harkins[1] has offered approximate calculations by applying a variety of estimations from conductivity methods to fairly dilute solutions.

It would seem, then, that the usual methods of studying ionization—colligative property and conductance methods—offer no satisfactory evidence concerning the ionic relationships of strong electrolytes, either singly or in mixtures, except in some cases in the region of extreme dilution.

3. Constitution of the Mercurial Phase.—The solid crystalline amalgams of the alkali and alkali-earth metals were long regarded as definite chemical compounds.[2] But after Ramsay's[3] measurements of the vapor-pressure changes produced by dissolving certain solid metals in mercury, the view-point gained prevalence that the liquid amalgams of the alkalies were mercurial solutions of these metals in the monatomic condition. A good many years later, however, definite evidence was brought forward which rendered this conclusion untenable, and we now know that the dilute liquid amalgams of the alkali and alkali-earth metals are mercurial solutions of intermetallic compounds of the general formula $MeHg_x$.[4]

But, since these amalgamated metals possess characteristic tendencies to enter aqueous solutions in the ionic condition, the hydrargyrides, even in dilute mercurial solution, must be regarded as being very slightly dissociated in the sense of the equation

$$MeHg_x \rightleftarrows Me + xHg.^5 \qquad (1)$$

[1] W. D. Harkins, *J. Am. Chem. Soc.*, **33**, 1868 (1911).

[2] For the bibliography, see *Z. anorg. Chem.*, **58**, 381 (1908).

[3] W. Ramsay, *J. Chem. Soc.*, **55**, 521 (1889).

[4] G. McP. Smith, *J. Am. Chem. Soc.*, **29**, 844 (1907); *Am. Chem. J.*, **36**, 124 (1906); **37**, 508 (1907); *Z. anorg. Chem.*, **58**, 381 (1908); *J. Am. Chem. Soc.*, **36**, 859 (1914); *Z. anorg. Chem.*, **88**, 161 (1914); *J. Am. Chem. Soc.*, **37**, 76 (1915). See also E. Beckmann and O. Liesche, *Z. anorg. Chem.*, **89**, 171 (1914).

[5] Cf. G. McP. Smith, *J. Am. Chem. Soc.*, **37**, 80, footnote 1 (1915).

B. Theoretical.

1. The Reversible Interaction Equilibrium.—When a liquid potassium amalgam is placed in contact with strontium chloride in aqueous solution, the potassium, owing to its solution tension, tends to pass into the solution in the ionic condition, and there results a difference of potential between the amalgam and the aqueous solution. The amalgam becomes negatively charged and attracts the positive ions of the solution, and, in case impurities are not present, strontium ions alone are discharged into the amalgam; this action continues until the solution tension of the strontium in the amalgam has assumed a value sufficiently great to prevent the further entrance of strontium from the aqueous solution. At this point, equilibrium is established. This reaction has been shown to be reversible,[1] so that if an equal weight of strontium amalgam of the same equivalent concentration is placed in contact with an equal volume of an equivalent solution of potassium chloride, the opposite reaction will take place, with the establishment of the same equilibrium. That is, the two amalgams at equilibrium will show the same ratio of metal concentrations and the total concentration in metal equivalents will be identical with the initial concentration, and the same is true of the two aqueous salt mixtures. Therefore, the reversible reaction may be represented by the expression

$$2\,K_{Hg} + Sr_{H_2O} \rightleftarrows Sr_{Hg} + 2K_{H_2O},$$

or, since only the free atoms and the ions of the metals are supposed to take a direct part in the reaction,

$$2K + Sr^{++} \rightleftarrows Sr + 2K^{+}. \qquad (2)$$

The free energy decrease attending the transfer, at the temperature T, of that quantity of a substance which is N moles in the state of a perfect gas, from an infinite quantity of a solution in which its vapor pressure is p_1 into an infinite quantity of another solution in which its vapor pressure is p_2 is

$$-\Delta F = NRT \log_e p_1/p_2,$$

or when, in conformity either with Raoult's or with Henry's law, the vapor pressures are proportional to the mol fractions, x_1 and x_2,

$$-\Delta F = NRT \log_e x_1/x_2.$$

The free energy decrease attending the transfer, at the temperature T, of one atom of strontium from dilute mercurial solution to the ionic state in an aqueous solution is, therefore,

$$-\Delta F = RT \log_e f\mathrm{Sr}/f'\mathrm{Sr}^{++},$$

in which fSr and $f'\mathrm{Sr}^{++}$ represent the respective fugacities of the uncombined strontium atom in mercurial solution and of the strontium ion in aqueous solution. The fugacity, or "corrected vapor pressure," of Lewis

[1] G. McP. Smith, *Am. Chem. J.*, **37**, 520 (1907).

is a measure of the tendency of a molecular species to escape from a particular thermodynamic environment which surrounds it in solution, into that condition of zero thermodynamic environment which prevails in a perfect gas. In the similar transfer of two atoms of potassium, we have

$$-\Delta F' = 2RT \log_e \frac{f_1\mathrm{K}}{f'_1\mathrm{K}^+} = RT \log_e \frac{(f_1\mathrm{K})^2}{(f'_1\mathrm{K}^+)^2}.$$

Since, at equilibrium, the two attendant free energy decreases are equal, it therefore follows that, at equilibrium,

$$\frac{f[\mathrm{Sr}].(f'_1[\mathrm{K}^+])^2}{(f_1[\mathrm{K}])^2.f'[\mathrm{Sr}^{++}]} = 1. \qquad (3)$$

In the case of individual metals, the Gibbs-Helmholz equation has been used to calculate the difference of potential which exists between mercurial solutions of different concentration when connected by an electrolyte containing ions of the metal:

$$E = \frac{RT}{nF} \log_e \frac{c_1}{c_2},$$

in which E is the potential difference between the two solutions, R the gas constant, T the absolute temperature, and n the valence of the ion of the metal, F is the value of the Faraday equivalent, and c_1 and c_2 are the concentrations of the two mercurial solutions. This equation has been found to hold the more accurately the greater the dilution; an increasing deviation takes place with increasing concentration.[1] The investigations of J. H. Hildebrand[2] and of Beckmann and Liesche[3] also indicate that ideal solution laws may properly be applied to dilute amalgams. This conclusion is fully borne out in the present investigation.

From the computations of Bates[4] on the partial osmotic pressures of the ions and of the non-ionized molecules of potassium chloride, and from the electromotive force measurements of MacInnes and Parker[5] on potassium chloride concentration cells, it may be shown that even in fairly concentrated solutions the fugacity of an ion species is *approximately* proportional to its concentration, *as determined by conductivity*, and that it is the fugacity of the non-ionized molecules that changes rapidly with increasing concentration.[6]

Assuming, then, that the ratio of the fugacities of two ions in mixtures varies directly as the ratio of the *true* ionic concentrations, *not necessarily*

[1] G. A. Hulett and R. E. DeLury, *J. Am. Chem. Soc.*, **30**, 1812 (1910); J. L. Crenshaw, *J. Phys. Chem.*, **14**, 158 (1910).

[2] J. H. Hildebrand, *Trans. Am. Elec. Soc.*, **22**, 319 (1912); *J. Am. Chem. Soc.*, **35**, 501 (1913).

[3] *Loc. cit.*

[4] S. J. Bates, *J. Am. Chem. Soc.*, **37**, 1428 (1915).

[5] D. A. MacInnes and K. Parker, *Ibid.*, **37**, 1456 (1915).

[6] Cf. R. C. Tolman and A. L. Ferguson, *Ibid.*, **34**, 232 (1912).

those determined by conductivity, and replacing the values of the fugacities of the metal atoms in the mercurial solution by the atomic fractions of the amalgamated metals, both free and combined, since we are in ignorance concerning their degrees of dissociation, Equation 3 becomes

$$\frac{(Sr_{Hg})\,(K^+)^2}{(K_{Hg})^2\,(Sr^{++})} = C_o, \qquad (4)$$

which, on the assumption that the two hydrargyrides do not interact, but that each dissociates in the presence of the other in accordance with Equation 1, is merely a "makeshift mass-law expression" for the equilibrium represented by Equation 2.

The amalgamated metal fractions of Equation 4 may be obtained from the analytical data of the equilibrium amalgams, but the ion fractions can only be calculated after the value of C_o has been determined. However, at any specific (very low) total amalgam concentration, under any particular conditions of salt concentration c, we may readily obtain the value of the expression

$$\frac{(Sr_{Hg})\,(K_{H_2O})^2}{(K_{Hg})^2\,(Sr_{H_2O})} = \frac{(Sr_{Hg})\,(K\text{-salt})^2}{(K_{Hg})^2\,(Sr\text{-salt})} = C_c, \qquad (5)$$

a value which, of course, applies only to those particular conditions.

Now, in any individual mixed salt solution, the ratio of the salt fractions must bear some numerical relationship to the ion-fraction ratio, or

$$\frac{(K\text{-salt})^2}{(Sr\text{-salt})} = n\,\frac{(K^+)^2}{(Sr^{++})}, \qquad (6)$$

in which the value of n is unknown and may, of course, vary with the conditions of salt concentration.[1] But, whatever the value of n may be at any specific composition of the mixture, it follows from the preceding equations that, in the case of any particular equilibrium mixture,

$$\frac{(Sr_{Hg})}{(K_{Hg})^2} = C_c\,\frac{(Sr\text{-salt})}{(K\text{-salt})^2} = \frac{C_c(Sr^{++})}{n\,(K^+)^2} = C_o\,\frac{(Sr^{++})}{(K^+)^2}.$$

That is, in the case of each individual equilibrium mixture, we have the relationship

[1] It was previously thought that the value of n would approach unity as a limit as the salt solution was made more and more dilute; because at infinite dilution the salts would be completely ionized, and the salt-concentration ratio would become the ion-concentration ratio. This conception is of no value, however, in the present work, unless the hydrated (and saltated) ions, as well as the simple unhydrated ions of the metals, take a direct part in the reaction of Equation 2. This is probably not the case, and if, as is almost certain, the equilibrium constants of the reactions $K^+ + xH_2O = [K(H_2O)_x]^+$ and $Sr^{++} + yH_2O = [Sr(H_2O)_y]^{++}$ are different, the value of n would never become equal to unity, but to γ^2/δ, in which γ and δ are the degrees of dissociation of the hydrated ions of potassium and strontium, respectively, into the simple ions and water. An extrapolation of the C_c values to infinite dilution would have no value, therefore, even if it could be successfully carried out.

$$\frac{(K^+)^2}{(Sr^{++})} = \frac{C_o\,(\text{K-salt})^2}{C_c\,(\text{Sr-salt})} = a, \qquad (7)$$

and, since the concentrations are expressed in terms of mol fractions,

$$(Sr^{++}) + (K^+) = 1, \qquad (8)$$

we have in (7) and (8) simultaneous equations, in which the unknown quantities are the strontium and potassium ion fractions.

Substituting the value $1 - (K^+)$ for (Sr^{++}) in Equation 7, we obtain

$$(K^+) = (-a + \sqrt{a^2 + 4a})/2; \qquad (9)$$

so that, if the value of C_o could be determined, we should be in a position to calculate the (simple) ion fractions of the metals in the individual mixed salt solutions.

2. The Mercurial Phase and the Mass Law.—A metal in dilute mercurial solution exerts a solution tension or tendency to pass into the ionic condition when the amalgam is brought in contact with an aqueous salt solution. This tendency is some function of the metal itself and of the mercurial environment in which it is placed. In the sense of Equation 1, a specific concentration of metal hydrargyride yields a specific concentration of free atoms of the metal, and consequently leads to a specific solution tension.

The mass-law expression for a reaction taking place in accordance with Equation 1 is

$$\frac{[Me]\,[Hg]^x}{[MeHg_x]} = \text{const.} \qquad (10)$$

But, since the amalgams are all extremely dilute and the solvent in which the equilibrium exists is mercury, the concentration of the mercury may be taken as constant, and we obtain

$$\frac{[Me]}{[MeHg_x]} = K_{Me}, \text{ or } \frac{\alpha}{1-\alpha} = K_{Me}, \qquad (11)$$

in which α is the degree of dissociation of the hydrargyride; whence it follows that

$$\alpha = \frac{K_{Me}}{1 + K_{Me}}. \qquad (12)$$

That is to say, if the mass law holds within the mercurial solution of a single hydrargyride, then the degree of dissociation of the hydrargyride remains constant so long as the solution is very dilute; and the concentration of the uncombined atoms of the metal is directly proportional to the hydrargyride concentration; the solution tension is a linear function of the amalgam concentration.

When any amalgam has been brought into equilibrium with a particular mixed salt solution, the total (combined and uncombined) concentration of each metal has been forced to adapt itself in such a way that the solu-

tion tension of each metal is zero with respect to the particular ion with which it is in equilibrium. Therefore, we have, at equilibrium,

$$\frac{[Sr^{\circ}_{Hg}]}{[Sr^{++}]} = \frac{[K^{\circ}_{Hg}]^2}{[K^{+}]^2},$$

in which $[Sr^{\circ}_{Hg}]$ and $[K^{\circ}_{Hg}]$ represent the free-atom concentrations of the metals in the mercurial phase; and the equilibrium constant between the atoms in the mercurial phase and the ions in the aqueous phase is unity:

$$\frac{[Sr^{\circ}_{Hg}][K^{+}]^2}{[K^{\circ}_{Hg}]^2[Sr^{++}]} = \frac{(Sr^{\circ}_{Hg})(K^{+})^2}{(Sr^{++})(K^{\circ}_{Hg})^2} = 1 \qquad (13)$$

From this it necessarily follows that

$$(Sr^{\circ}_{Hg}) = (Sr^{++}) \quad \text{and} \quad (K^{\circ}_{Hg}) = (K^{+}),$$

or, *the free-atom fractions in the mercurial phase are identical in value with the ion fractions in the aqueous phase for each individual metal at equilibrium.*[1]

It has been assumed, on the basis of the mass law and of what is known concerning the behavior of mercurial solutions, that, in the case of these dilute liquid amalgams, α = const. for one hydrargyride, and β = const. for some other hydrargyride. Now if the mass law is applicable to each of the two equilibria,

$$Me + x\ Hg \rightleftarrows MeHg_x$$

and

$$Me' + y\ Hg \rightleftarrows Me'Hg_y,$$

and in the presence of the other, it must necessarily follow that

$$\alpha/\beta = \text{const.} \qquad (14)$$

In equilibria between identical mixed aqueous solutions and amalgams of different total equivalent concentration, any difference in degree of dissociation which exists between the two hydrargyrides will be manifested by differences in the C_e values (Equation 5). Because, owing to the constant value in this series of the expression (K-salt)^2/(Sr-salt), the values of $(K^{+})^2/(Sr^{++})$ are also constant (Equation 6), and therefore those of $(Sr^{\circ}_{Hg})/(K^{\circ}_{Hg})^2$ (Equation 13). The only values which may vary with the amalgam concentration in such a series are those of the total-atom fractions of strontium and potassium in the dilute amalgams; and at each amalgam concentration these must be adjusted in such a way that, without changing the total equivalent concentration of the amalgam, (Sr°_{Hg}) and (K°_{Hg}) may be equal to (Sr^{++}) and to (K^{+}), respectively (Equation 13). Moreover, if the values of $(Sr^{\circ}_{Hg})/(K^{\circ}_{Hg})^2$ are identical in the different amalgams of the series, then the values of $(Sr_{Hg})/(K_{Hg})^2$ must vary with the total amalgam concentration, unless, through a rare

[1] In this paper, actual concentrations are denoted by square brackets, while mol-fractional concentrations are indicated by means of parentheses.

coincidence, the degrees of dissociation of the two hydrargyrides were equal.

If α and β are constant and unequal in value (Equations 12 and 14), then the value of $(Sr_{Hg})/(K_{Hg})^2$, and therefore that of C_c, in the amalgam concentration series under discussion should be a linear function of the amalgam concentration. This has been found to be true in the case of the more dilute amalgams, but at concentrations above 2 milli-equivalents of metals per 100 g. of mercury a deviation from the straight line becomes apparent.

C. Materials, Apparatus and Method of Experimentation.

1. Materials.

The decomposition of the amalgams by the water of the salt solutions is catalyzed by dust particles on the surface of the mercury or by heavy metals contaminating the solution or the amalgam. It is imperative in this work to use only the purest of materials.

(*a*) **Water, Mercury, Potassium Chloride and Strontium Chloride.**—These materials were purified according to methods already described in the preceding papers of this series.[1]

(*b*) **Amalgams.**—The amalgams were prepared by the electrolysis of saturated salt solutions, as described by Smith and Bennett.[2] Fairly concentrated liquid amalgams were prepared and analyzed. Before use they were diluted with mercury to the specific concentration desired.

(*c*) **Ammonium Carbonate.**—A sample of the best grade commercially obtainable was used. Upon the ignition of 5 g. of the salt in a platinum dish, no residue whatever remained.

(*d*) **Hydrochloric Acid.**—Gaseous hydrogen chloride, from table salt and pure sulfuric acid, was passed into distilled water.

2. Apparatus.

A description of the apparatus used in this investigation may be found in the paper of Smith and Ball, to which reference has already been made.

3. Method of Experimentation.

(*a*) **Solutions.**—Separate solutions of potassium chloride and strontium chloride were made up, each equal in concentration to the total equivalent concentration desired for the mixed salt solution. By bringing together these solutions in the proper volume relations, in bottles of "Resistenz" glass, mixtures were easily prepared of the specific salt-concentration ratio desired.

The pure dry potassium chloride was weighed out in calculated quantities, dissolved in pure water, transferred to calibrated volumetric flasks, and diluted to the mark at 25°.

[1] Smith and Ball, and Smith and Braley, *Loc. cit.*

[2] G. McP. Smith and H. C. Bennett, *J. Am. Chem. Soc.* **31**, 802 (1909).

The hydrated strontium salt, $SrCl_2.6H_2O$, was weighed out in sufficient quantity to give a solution slightly more concentrated than that desired. This amount was dissolved in water, diluted to a sufficient volume, and the normality determined by the Volhard volumetric method for chlorine, the silver chloride being filtered off before titration. The standardized solution of the salt was then accurately diluted to the normality desired.

(*b*) **Equilibrium.**—In order in each run to start with amalgams having as nearly as possible the same equivalent concentration, the analyzed stock amalgams were diluted with mercury to the concentration decided upon. The mercury for dilution was weighed out, to within about 0.2 g., upon a small trip balance, and transferred to the reaction flask; 50 cc. of the mixed salt solution was added, and the whole counterpoised on the trip balance; finally, the calculated quantity of the liquid stock amalgam was added. The flask containing the reaction mixture was at once placed in the thermostat and shaken for 15 minutes, after which the solution was decanted from the amalgam; a fresh portion of the solution was immediately added, the flask again shaken for 15 minutes in the thermostat, and the solution again decanted. If the aqueous solution was very dilute, the amalgams were treated in this way with 10 successive portions of the solution; in most cases only 6 renewals were required; and with the most concentrated solutions still fewer renewals were necessary to produce the desired equilibrium.

After decanting the last portion of the solution, the amalgam was washed with water, and decomposed with hydrochloric acid, as described in the earlier papers. Each run was made with 6 separate reaction mixtures, 3 of which were started with potassium amalgam and 3 with strontium amalgam, the aqueous solution being identical in all 6 cases. In each run, therefore, equilibrium was approached 3 times from each side.

(*c*) **Treatment of the Decomposition Products.**—The hydrochloric acid extract containing the potassium and strontium from the equilibrium amalgam was in each case quantitatively withdrawn from the mercury in the decomposition flask, evaporated to dryness in a platinum dish on the steam bath, and the residue analyzed for strontium and potassium. The mercury itself was dried and weighed to within 0.2 g.

(*d*) **Determination of the Strontium and Potassium.**—The acid-free mixed chloride residue was dissolved in about 50 cc. of water, the solution treated with dil. sulfuric acid in a slight excess, and to the whole an equal volume of alcohol added. This mixture was allowed to stand, usually over night, and then it was filtered through an asbestos-matted Gooch crucible, washed thoroughly with 50% alcohol containing a little sulfuric acid, and finally with pure alcohol. The crucible containing the strontium sulfate was dried in an electric oven, and then ignited inside a larger

crucible provided with an asbestos ring, so as to maintain an air bath around the precipitate during ignition.

The alcoholic filtrate and washings from the strontium sulfate were evaporated to a small volume, transferred to a weighed platinum dish and evaporated to dryness. Ammonium carbonate was lightly scattered over the surface of the residue, to facilitate the removal of the excess of sulfuric acid, and the whole was then ignited at a temperature not exceeding dull redness.

Test analyses, with salt mixtures of known composition, gave results which were entirely satisfactory.

D. Experimental Data.

The data obtained in this investigation are recorded in the following tables. Unless otherwise stated, the figures in the first column in each table refer to the number of the experiment; the second column indicates the amalgam used at the start; the third, fourth, and fifth columns contain the quantities in grams obtained in the analysis of the equilibrium amalgam; Col. 6 shows the concentration of the amalgam, at equilibrium, in total milli-equivalents of amalgamated metals per 10 g. of mercury, as calculated from the analytical data; Cols. 7 and 8 contain the amalgamated metal fractions in the equilibrium amalgam, as calculated from Cols. 3 and 4; and Col. 9 gives the value of the expression

$$\frac{(\mathrm{Sr_{Hg}})\,(\text{K-salt})^2}{(\mathrm{K_{Hg}})^2\,(\text{Sr-salt})} = C_c,$$

in which $(\mathrm{Sr_{Hg}})$ and $(\mathrm{K_{Hg}})$ are the respective *amalgamated metal fractions* in the mercurial phase, from Cols. 7 and 8, and (K-salt) and (Sr-salt) are the *mol fractions* of the salts in the aqueous phase. Since the C_c value thus obtained is found to be a linear function of the amalgam concentration, expressed in total milli-equivalents of amalgamated metals per 10 g. of mercury, it is possible to correct these values to some specific amalgam concentration; Col. 10 contains these corrected values.[1] The individual values in each set of experiments were corrected in every case by a simple proportion, to the average equilibrium-amalgam concentration of that set.

1. **Effect of Varying the Concentration of the Mercurial Phase at a Fixed (Equivalent) Salt-Concentration Ratio and a Fixed Normal Concentration of the Aqueous Phase.**—In the case of the sodium-potassium equilibrium, and also of the sodium-strontium equilibrium, it has previously been observed that changes in the total concentration of the mercurial phase exert a decided effect upon the value of C_c. In the case of the sodium-strontium equilibrium, for example, with aqueous phases of fixed normal concentration containing sodium and strontium chlorides in equivalent quantities, Smith and Braley[2] found the C_c value to be a linear function

[1] Cf. Smith and Braley, *J. Am. Chem. Soc.* **39**, 1553f (1917).

[2] *Loc. cit.*

of the amalgam concentration. Similar results have been obtained in the present investigation, in which equivalent salt mixtures have been studied at 0.1 *N*, 0.2 *N*, 0.4 *N*, 0.8 *N*, 1.6 *N*, and at 3.0 *N* total salt concentration. The data of these experiments are contained in Tables II, III, IV, V, VI and VII. In addition, Table I includes the data for a 0.05 *N* mixture; in this case only one run of 12 experiments was made, but since C_c was found to be a linear function of the amalgam concentration at each of the other salt concentrations, it is assumed to be so also at this concentration.

TABLE I.

Mixed Aqueous Phase 0.05 *N*. KCl : $\frac{1}{2}$ $SrCl_2$.

Temperature 25°.

No.	Amal. at start.	Analysis of the equilibrium amalgam. K_2SO_4.	$SrSO_4$.	Hg.	Milli-equivs. of metals per 10 g. Hg.	Amalgamated metal fractions. K.	Sr.	Cc.	Cc. corr. to 0.0684. mg. equiv.
1.....	Sr	0.0469	0.2021	391.9	0.0700	0.3291	0.6709	8.25	8.07
2.....	Sr	0.0494	0.2166	387.6	0.0755	0.3252	0.6748	8.50	7.70
3.....	Sr	0.0499	0.2319	396.4	0.0782	0.3122	0.6878	9.39	8.22
4.....	K	0.0461	0.1919	406.3	0.0644	0.3364	0.6636	7.81	8.29
5.....	K	0.0499	0.2059	408.9	0.0688	0.3381	0.6619	7.71	7.67
6.....	K	0.0474	0.1954	395.8	0.0676	0.3386	0.6614	7.68	7.77
7.....	Sr	0.0476	0.1951	400.4	0.0667	0.3402	0.6598	7.59	7.78
8.....	Sr	0.0517	0.2331	410.5	0.0708	0.3393	0.6607	7.65	7.39
9.....	Sr	0.0508	0.2343	408.0	0.0768	0.3138	0.6862	9.28	8.26
10.....	K	0.0450	0.1862	397.1	0.0641	0.3376	0.6624	7.74	8.26
11.....	K	0.0440	0.1634	402.8	0.0567	0.3628	0.6372	6.45	7.78
12.....	K	0.0460	0.1803	406.0	0.0614	0.3494	0.6506	7.10	7.92
Mean.....					0.0684				7.93

TABLE II.

Mixed Aqueous Phase 0.10 *N*.

									Corr. to 0.1401.
1.....	Sr	0.0566	0.2364	205.1	0.1571	0.3355	0.6645	7.86	7.02
2.....	Sr	0.0555	0.2247	204.8	0.1506	0.3423	0.6577	7.48	6.96
3.....	Sr	0.0536	0.2140	201.3	0.1464	0.3459	0.6541	7.28	6.97
4.....	K	0.0469	0.1622	192.1	0.1200	0.3792	0.6208	5.75	6.72
5.....	K	0.0493	0.1843	200.0	0.1285	0.3603	0.6397	6.56	7.16
6.....	K	0.0533	0.2044	205.1	0.1383	0.3545	0.6455	6.84	6.92
Mean.....					0.1401				6.96
									Corr. to 0.0743.
7.....	Sr	0.0704	0.1753	399.4	0.0680	0.4585	0.5415	3.42	3.74
8.....	Sr	0.0793	0.2188	402.8	0.0817	0.4334	0.5666	4.02	3.67
9.....	Sr	0.0801	0.2377	407.8	0.0860	0.4156	0.5844	4.50	3.89
10.....	K	0.0724	0.1788	405.7	0.0685	0.4605	0.5395	3.39	3.68
11.....	K	0.0697	0.1800	405.6	0.0680	0.4497	0.5503	3.62	3.96
12.....	K	0.0730	0.2002	410.0	0.0737	0.4349	0.5651	3.98	4.01
Mean.....					0.0743				3.83

The values of C_e, as ordinates, are plotted against the total amalgam concentration in milli-equivalents of metals per 10 g. of mercury, in Fig. 1. Each point indicated in the plot is the average of about 6 corrected C_e values. It will be noted, in Tables III and IV, that the values of C_e for the more concentrated amalgams are not very concordant; and also, in Fig. 1, that the average values for these amalgams do not fall upon the

TABLE III.

Mixed Aqueous Phase 0.20 *N*. KCl : $^1/_2$ $SrCl_2$.

Temperature 25°.

No.	Amal. at start.	Analysis of the equilibrium amalgam. K_2SO_4.	$SrSO_4$.	Hg.	Milli-equivs. of metals per 10 g. Hg.	Amalgamated metal fractions. K.	Sr.	Cc.	Cc. corr. to 0.6138 mg. equiv.
1.....	Sr	0.0752	0.4886	98.7	0.6265	0.2453	0.7547	16.7	16.3
2.....	Sr	0.0738	0.4585	98.5	0.5928	0.2532	0.7468	15.5	16.0
3.....	Sr	0.0749	0.4612	98.2	0.5987	0.2551	0.7449	15.2	15.6
4.....	K	0.0691	0.4733	96.3	0.6174	0.2353	0.7647	18.4	18.3
5.....	K	0.0758	0.5069	102.8	0.6213	0.2396	0.7604	17.7	17.4
6.....	K	0.0734	0.4999	100.4	0.6259	0.2362	0.7638	18.2	17.9
Mean.....					0.6138				16.9
									Corr. to 0.3111.
7.....	Sr	0.0591	0.2480	102.3	0.3303	0.3342	0.6658	7.94	7.48
8.....	Sr	0.0667	0.3049	108.7	0.3758	0.3154	0.6846	9.17	7.59
9.....	Sr	0.0613	0.2590	103.2	0.3414	0.3328	0.6672	8.02	7.30
10.....	K	0.0514	0.1860	103.6	0.2525	0.3685	0.6315	6.19	7.62
11.....	K	0.0586	0.2206	106.8	0.2879	0.3591	0.6409	6.62	7.17
12.....	K	0.0555	0.2113	105.4	0.2788	0.3562	0.6438	6.77	7.55
Mean.....					0.3111				7.45
									Corr. to 0.1805.
13.....	Sr	0.0894	0.2615	202.3	0.1914	0.4188	0.5812	4.41	4.16
14.....	Sr	0.0868	0.2505	203.9	0.1827	0.4223	0.5777	4.32	4.27
15.....	Sr	0.0952	0.2935	207.1	0.2070	0.4059	0.5941	4.81	4.18
16.....	K	0.0855	0.2334	209.1	0.1685	0.4360	0.5640	3.95	4.23
17.....	K	0.0893	0.2511	209.0	0.1800	0.4285	0.5715	4.15	4.17
18.....	K	0.0804	0.2031	204.2	0.1535	0.4549	0.5451	3.51	4.13
Mean.....					0.1805				4.19
									Corr. to 0.1511.
19.....	Sr	0.0741	0.1754	192.6	0.1433	0.4716	0.5284	3.17	3.34
20.....	K	0.0737	0.1875	192.0	0.1504	0.4534	0.5466	3.54	3.55
21.....	K	0.0864	0.2214	213.2	0.1596	0.4515	0.5485	3.58	3.39
Mean.....					0.1511				3.43
									Corr. to 0.0676.
22.....	Sr	0.0999	0.1779	396.0	0.0778	0.5440	0.4560	2.05	1.78
23.....	Sr	0.1061	0.1914	398.3	0.0829	0.5408	0.4592	2.09	1.70
24.....	K	0.0921	0.1243	382.6	0.0630	0.6093	0.3907	1.40	1.51
25.....	K	0.0910	0.1231	388.4	0.0614	0.6095	0.3905	1.40	1.54
26.....	K	0.0795	0.1069	400.2	0.0526	0.6107	0.3893	1.39	1.79
Mean.....					0.0676				1.66

line connecting the values obtained in the case of the more dilute amalgams. A similar disagreement in the data for the more concentrated amalgams was observed by Smith and Ball in the sodium-potassium study, and by Smith and Braley in the sodium-strontium equilibrium.

TABLE IV.

Mixed Aqueous Phase 0.40 *N*. KCl : $\frac{1}{2}$ $SrCl_2$.

Temperature 25°.

No.	Amal. at start.	Analysis of the equilibrium amalgam. K_2SO_4.	$SrSO_4$.	Hg.	Milli-equivs. of metals per 10 g. Hg.	Amalgamated metal fractions. K.	Sr.	Cc.	Cc. corr. to 0.6339 mg. equiv.
1.....	Sr	0.0577	0.2731	53.0	0.6859	0.3083	0.6917	9.68	8.93
2.....	Sr	0.0646	0.2620	67.0	0.5363	0.3422	0.6578	7.49	8.84
3.....	Sr	0.0565	0.2685	53.6	0.6664	0.3077	0.6923	9.73	9.50
4.....	K	0.0538	0.2473	52.3	0.6330	0.3150	0.6850	9.20	9.22
5.....	K	0.0520	0.2352	49.0	0.6444	0.3175	0.6825	9.02	8.87
6.....	K	0.0581	0.2595	54.8	0.6376	0.3208	0.6792	8.79	8.72
Mean.....					0.6339				9.01
									Corr. to 0.5327.
7.....	Sr	0.0871	0.3147	99.5	0.4449	0.3685	0.6315	6.19	7.42
8.....	Sr	0.0933	0.4169	99.0	0.5667	0.3208	0.6792	8.78	8.23
9.....	K	0.0957	0.3972	98.4	0.5511	0.3372	0.6628	7.77	7.51
10.....	K	0.0985	0.3848	99.3	0.5357	0.3505	0.6495	7.05	7.02
11.....	K	0.0979	0.4211	101.0	0.5651	0.3288	0.6712	8.27	7.78
Mean.....					0.5327				7.59
									Corr. to 0.3176.
12.....	Sr	0.0677	0.1714	99.5	0.2655	0.4547	0.5453	3.51	4.19
13.....	Sr	0.0793	0.2305	100.8	0.3392	0.4205	0.5795	4.36	4.08
14.....	Sr	0.0696	0.1807	104.8	0.2629	0.4478	0.5522	3.67	4.42
15.....	Sr	0.0754	0.2119	98.0	0.3237	0.4283	0.5717	4.16	4.08
16.....	K	0.0779	0.2247	100.3	0.3332	0.4225	0.5775	4.31	4.11
17.....	K	0.0649	0.1856	81.8	0.3339	0.4242	0.5758	4.26	4.05
18.....	K	0.0948	0.2931	107.8	0.3972	0.4057	0.5943	4.81	3.85
19.....	K	0.0711	0.1856	99.8	0.2843	0.4468	0.5532	3.69	4.12
Mean.....					0.3176				4.11
									Corr. to 0.1730.
20.....	Sr	0.1252	0.2632	197.7	0.2176	0.5008	0.4992	2.65	2.11
21.....	Sr	0.1179	0.2229	204.0	0.1852	0.5272	0.4728	2.26	2.11
22.....	Sr	0.1153	0.2135	204.4	0.1785	0.5327	0.4673	2.20	2.13
23.....	K	0.0940	0.1567	201.1	0.1384	0.5586	0.4414	1.88	2.35
24.....	K	0.0997	0.1675	204.5	0.1455	0.5568	0.4432	1.90	2.26
Mean.....					0.1730				2.19
									Corr. to 0.0881.
25.....	Sr	0.1440	0.1851	394.0	0.0931	0.6211	0.3789	1.31	1.24
26.....	Sr	0.1700	0.2410	417.2	0.1097	0.5980	0.4020	1.49	1.20
27.....	Sr	0.1519	0.1832	398.9	0.0937	0.6361	0.3639	1.20	1.13
28.....	K	0.1251	0.1363	399.0	0.0732	0.6595	0.3405	1.04	1.25
29.....	K	0.1285	0.1478	393.8	0.0784	0.6471	0.3529	1.12	1.26
30.....	K	0.1340	0.1523	398.4	0.0803	0.6501	0.3499	1.10	1.21
Mean.....					0.0881				1.22

In any one run, the equilibrium amalgams of the individual mixtures were always found to differ somewhat in concentration; because, in the first place, the stock amalgams were weighed out more or less roughly for dilution, and, in the second place, the evolution of hydrogen (always in evidence to a slight extent, at best) varied somewhat in the individual experiments.

TABLE V.

Mixed Aqueous Phase 0.80 *N*. KCl : ½ $SrCl_2$.

Temperature 25°.

No.	Amal. at start.	Analysis of the equilibrium amalgam. K_2SO_4.	$SrSO_4$.	Hg.	Milli-equivs. of metals per 10 g. Hg.	Amalgamated metal fractions. K.	Sr.	Cc.	Cc. corr. to 0.6779 mg. equiv.
1.....	Sr	0.1420	0.4361	99.4	0.6416	0.4063	0.5937	4.79	5.07
2.....	Sr	0.1474	0.4834	97.3	0.7149	0.3916	0.6084	5.28	5.01
3.....	Sr	0.1477	0.4954	101.0	0.7020	0.3859	0.6141	5.49	5.30
4.....	K	0.1423	0.5145	101.0	0.7165	0.3685	0.6315	6.18	5.85
5.....	K	0.1407	0.4328	101.5	0.6235	0.4069	0.5931	4.77	5.19
6.....	K	0.1415	0.4620	99.5	0.6687	0.3924	0.6076	5.26	5.33
Mean.....					0.6779				5.35
									Corr. to 0.3240.
7.....	Sr	0.1086	0.2449	104.5	0.3746	0.4835	0.5165	2.94	2.54
8.....	Sr	0.1037	0.2345	102.0	0.3670	0.4829	0.5171	2.96	2.61
9.....	K	0.0868	0.1697	99.6	0.2856	0.5192	0.4808	2.37	2.69
10.....	K	0.1058	0.2159	101.6	0.3509	0.5082	0.4918	2.54	2.35
11.....	K	0.0810	0.1395	101.3	0.2418	0.5508	0.4492	1.97	2.65
Mean.....					0.3240				2.57
									Corr. to 0.1678.
12.....	Sr	0.1255	0.1586	199.1	0.1590	0.6252	0.3748	1.28	1.35
13.....	Sr	0.1326	0.1647	205.1	0.1617	0.6291	0.3709	1.25	1.30
14.....	K	0.1341	0.1895	200.2	0.1800	0.5988	0.4012	1.49	1.39
15.....	K	0.1479	0.1865	212.7	0.1752	0.6259	0.3741	1.27	1.22
16.....	K	0.1455	0.1762	220.0	0.1631	0.6352	0.3648	1.20	1.23
Mean.....					0.1678				1.30

TABLE VI.

Mixed Aqueous Phase 1.60 *N*. KCl : ½ $SrCl_2$.

Temperature 25°.

									Corr. to 0.1729.
1.....	Sr	0.1360	0.1512	198.0	0.1620	0.6551	0.3449	1.07	1.14
2.....	Sr	0.1487	0.1656	199.6	0.1760	0.6545	0.3455	1.07	1.05
3.....	Sr	0.1498	0.1846	198.8	0.1876	0.6312	0.3688	1.23	1.13
4.....	K	0.1468	0.1866	201.4	0.1845	0.6240	0.3760	1.29	1.21
5.....	K	0.1355	0.1409	200.2	0.1542	0.6696	0.3304	0.98	1.10
Mean.....					0.1729				1.13
									Corr. to 0.0825.
6.....	Sr	0.1576	0.1405	400.2	0.0834	0.7031	0.2969	0.80	0.79
7.....	Sr	0.1710	0.1418	412.6	0.0850	0.7179	0.2821	0.73	0.71
8.....	Sr	0.1821	0.1567	403.2	0.0942	0.7104	0.2896	0.76	0.67
9.....	K	0.1568	0.1301	395.4	0.0813	0.7178	0.2822	0.73	0.74
10.....	K	0.1528	0.1307	398.8	0.0795	0.7116	0.2884	0.76	0.79
11.....	K	0.1401	0.1147	397.1	0.0719	0.7204	0.2796	0.72	0.82
Mean.....					0.0825				0.75

TABLE VII.

Mixed Aqueous Phase 3.00 *N*.

No.	Amal at start.	Analysis of the equilibrium amalgam. K_2SO_4.	$SrSO_4$.	Hg.	Milli-equivs. of metals per 10 g. Hg.	Amalgamated metal fractions. K.	Sr.	Cc.	Cc. corr. to 0.3505. mg. equiv.
1.....	Sr	0.1268	0.2158	106.6	0.3569	0.5534	0.4466	1.94	1.91
2.....	Sr	0.1068	0.2150	103.4	0.3448	0.5115	0.4885	2.48	2.52
3.....	Sr	0.1229	0.2471	101.7	0.4032	0.5122	0.4878	2.48	2.16
4.....	K	0.1090	0.2034	105.4	0.3287	0.5304	0.4696	2.22	2.36
5.....	K	0.1004	0.2207	103.7	0.3430	0.4897	0.5103	2.83	2.89
6.....	K	0.1056	0.1943	102.0	0.3264	0.5339	0.4661	2.18	2.34
Mean.....					0.3505				2.36

Fig. 1.—Showing value of C_c as a function of amalgam concentration at different total salt concentrations. Equivalent proportions of K and Sr in aqueous phase. Temp. 25°.

2. Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio and a Fixed Amalgam Concentration.—Table VIII contains data showing the effect of increasing the total salt concentration in stages from 0.05 N to 3.00 N—the salts being present in equivalent proportions—at various fixed amalgam concentrations. The values of C_c in this table were obtained by simply reading them from the plots in Fig. 1, at the indicated amalgam concentrations. The values in parenthesis were obtained by extrapolation of the lines beyond the regions covered by experimental data. Fig. 2 illustrates the effect upon the C_c value, at different specific amalgam concentrations, of varying the normality of the aqueous phase in the

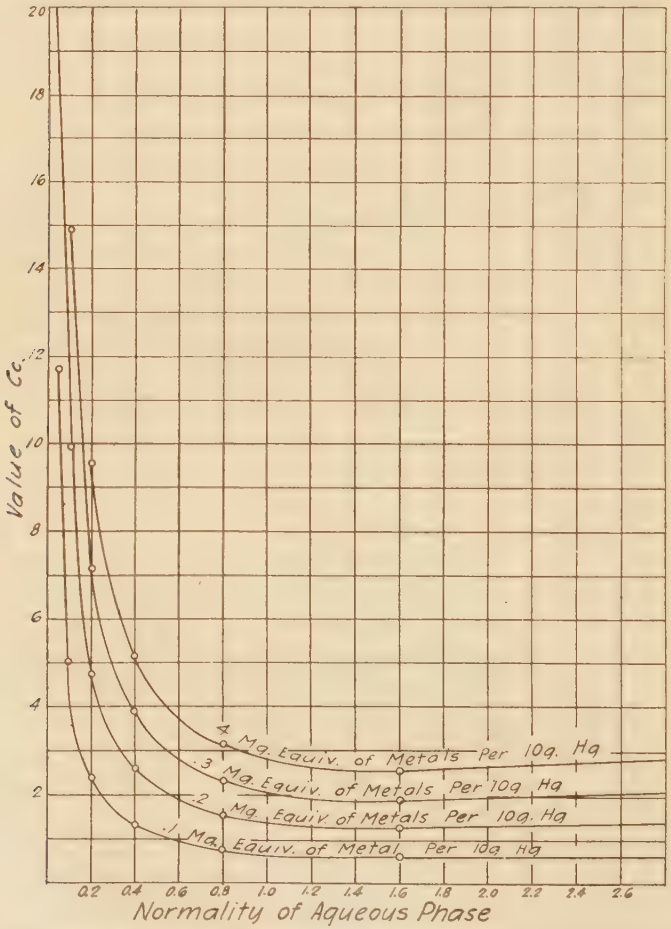

Fig. 2.—Showing value of C_c as a function of total salt concentration at different amalgam concentrations. Equivalent proportions of K and Sr in aqueous phase. Temp. 25°.

TABLE VIII.

Showing the Value of C_c as a Function of Total Salt Concentration at a Fixed (Equivalent) Salt-Concentration Ratio and at Various Specific Amalgam Concentrations at 25°.

Normality of aqueous phase.	0.1 mg. equiv. of metal per 10 g. Hg.	0.2 mg. equiv. of metal per 10 g. Hg.	0.3 mg. equiv. of metal per 10 g. Hg.	0.4 mg. equiv. of metal per 10 g. Hg.
0.05	11.70	(23.40)	...	..
0.10	5.05	9.95	(14.90)	..
0.20	2.40	4.75	7.15	9.55
0.40	1.30	2.60	3.90	5.20
0.80	0.78	1.55	2.35	3.15
1.60	0.62	1.28	(1.90)	(2.55)
3.00	0.65	1.35	2.05	(2.70)

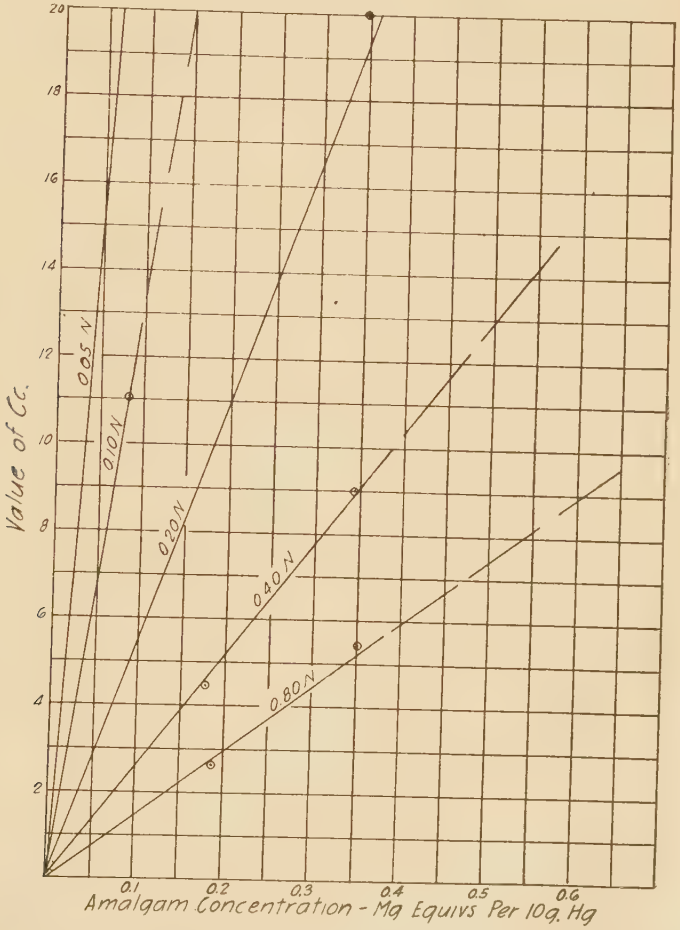

Fig. 3.—Showing value of C_c as a function of amalgam concentrations at various total salt concentrations. Equivalent proportions of K and Sr in aqueous phase. Temp. 40°.

case of equivalent salt mixtures. Upon comparing this effect with that illustrated in Fig. 1, it is clearly seen that of the two phases, as regards constitution, the aqueous is by far the more complex.

3. Effect of Changing the Temperature.—The experiments so far outlined were all performed at 25°. Similar studies were now undertaken at a temperature of 40°, primarily to determine whether a change of 15° would produce any notable difference in the ion-fraction changes of potassium and strontium in the aqueous phase. At 40° also, as shown by the data of Tables XI, XII, and XIII, and by Fig. 3, the value of C_c is a linear function of amalgam concentration in the case of a 0.2 N, a 0.4 N, or an 0.8 N aqueous phase. Data are given in Tables IX and X for 0.05 N and 0.1 N salt mixtures, each at a single amalgam concentration; but since C_c in all other cases is a linear function of amalgam concentration, it is assumed to be so in these cases, as well.

TABLE IX.

Mixed Aqueous Phase 0.05 N. KCl : $\frac{1}{2}$ $SrCl_2$.

Temperature 40°.

No.	Amal. at start.	Analysis of the equilibrium amalgam. K_2SO_4.	$SrSO_4$.	Hg.	Milli-equivs. of metals per 10 g. Hg.	Amalgamated metal fractions. K.	Sr.	Cc.	Cc. corr. to 0.0742.
1.....	Sr	0.0455	0.3175	507.2	0.0785	0.2319	0.7681	19.0	18.0
2.....	Sr	0.0456	0.3756	516.9	0.0892	0.2041	0.7959	25.4	21.1
3.....	Sr	0.0468	0.4155	514.2	0.0985	0.1918	0.8082	29.3	22.0
4.....	K	0.0354	0.2421	509.3	0.0598	0.2357	0.7643	18.3	22.6
5.....	K	0.0412	0.3066	511.9	0.0744	0.2209	0.7791	21.3	21.2
6.....	K	0.0409	0.3082	544.3	0.0704	0.2191	0.7809	21.7	22.8
7.....	Sr	0.0397	0.3075	502.0	0.0758	0.2138	0.7862	22.9	22.4
8.....	Sr	0.0445	0.3159	501.0	0.0789	0.2291	0.7709	19.6	18.4
9.....	Sr	0.0362	0.2564	507.1	0.0633	0.2300	0.7700	19.4	22.7
10.....	K	0.0362	0.2316	508.0	0.0579	0.2484	0.7516	16.2	20.8
11.....	K	0.0386	0.2787	504.2	0.0690	0.2258	0.7742	20.2	21.8
Mean.....					0.0742				21.2

TABLE X.

Mixed Aqueous Phase 0.10 N. KCl : $\frac{1}{2}$ $SrCl_2$.

Temperature 40°.

									Corr. to 0.0814.
1.....	Sr	0.0491	0.2442	406.7	0.0792	0.2973	0.7027	10.59	10.90
2.....	Sr	0.0478	0.2427	400.1	0.0797	0.2940	0.7060	10.88	11.10
3.....	Sr	0.0534	0.2830	407.7	0.0907	0.2848	0.7152	11.75	10.52
4.....	K	0.0480	0.2376	399.7	0.0785	0.2993	0.7007	10.42	10.82
5.....	K	0.0468	0.2446	400.9	0.0798	0.2875	0.7125	11.48	11.70
6.....	K	0.0482	0.2488	406.5	0.0803	0.2896	0.7104	11.28	11.42
Mean.....					0.0814				11.08

Table XI.

Mixed Aqueous Phase 0.20 *N*.

No.	Amal. at start.	Analysis of the equilibrium amalgam. K_2SO_4.	$SrSO_4$.	Hg.	Milli-equivs. of metals per 10 g. Hg.	Amalgamated metal fractions. K.	Sr.	Cc.	Cc. corr. to 0.3514. mg. equiv.
1.....	Sr	0.0372	0.2556	99.9	0.3214	0.2349	0.7651	18.47	20.20
2.....	Sr	0.0410	0.2931	107.9	0.3394	0.2277	0.7723	19.83	20.50
3.....	Sr	0.0410	0.2881	104.3	0.3459	0.2308	0.7692	19.24	19.60
4.....	K	0.0429	0.3149	109.1	0.3596	0.2235	0.7765	20.70	20.30
5.....	K	0.0401	0.3088	102.5	0.3730	0.2149	0.7851	22.64	21.30
6.....	K	0.0407	0.3017	102.0	0.3680	0.2217	0.7783	21.09	20.15
Mean.....					0.3514				20.34
									Corr. to 0.1642.
7.....	Sr	0.0552	0.2551	191.8	0.1780	0.3134	0.6866	9.31	8.58
8.....	Sr	0.0532	0.2404	198.9	0.1624	0.3183	0.6817	8.96	9.05
9.....	Sr	0.0536	0.2445	184.8	0.1774	0.3165	0.6835	9.08	8.42
10.....	K	0.0527	0.2435	201.1	0.1619	0.3139	0.6861	9.27	9.41
11.....	K	0.0523	0.2314	204.7	0.1525	0.3229	0.6771	8.64	9.30
12.....	K	0.0544	0.2238	199.9	0.1531	0.3388	0.6612	7.67	8.26
Mean.....					0.1642				8.84

Table XII.

Mixed Aqueous Phase 0.40 *N*. KCl : $\frac{1}{2}$ $SrCl_2$.

Temperature 40°.

									Corr. to 0.3444.
1.....	Sr	0.0590	0.2530	106.0	0.3239	0.3297	0.6703	8.22	8.75
2.....	Sr	0.0575	0.2418	102.6	0.3209	0.3339	0.6661	7.95	8.55
3.....	K	0.0587	0.2752	103.3	0.3554	0.3107	0.6893	9.51	9.20
4.....	K	0.0591	0.2745	101.2	0.3623	0.3120	0.6880	9.42	8.95
5.....	K	0.0582	0.2772	102.5	0.3596	0.3067	0.6933	9.81	9.38
Mean.....					0.3444				8.97
									Corr. to 0.1772.
6.....	Sr	0.0788	0.2169	199.2	0.1641	0.4341	0.5659	4.00	4.33
7.....	Sr	0.0787	0.2230	203.6	0.1636	0.4264	0.5736	4.16	4.51
8.....	Sr	0.0858	0.2529	205.0	0.1823	0.4170	0.5830	4.46	4.33
9.....	K	0.0836	0.2589	204.5	0.1848	0.4049	0.5951	4.84	4.64
10.....	K	0.0863	0.2663	203.6	0.1910	0.4057	0.5943	4.81	4.46
Mean.....					0.1772				4.45

Table XIII.

Mixed Aqueous Phase 0.80 *N*.

									Corr. to 0.3522.
1.....	Sr	0.0759	0.2353	104.1	0.3299	0.4051	0.5949	4.84	5.17
2.....	Sr	0.0766	0.2434	101.5	0.3478	0.3990	0.6010	5.03	5.10
3.....	Sr	0.0787	0.2615	109.0	0.3441	0.3881	0.6119	5.41	5.53
4.....	K	0.0804	0.2853	105.5	0.3820	0.3728	0.6272	6.01	5.53
5.....	K	0.0779	0.2716	107.9	0.3570	0.3771	0.6229	5.83	5.76
Mean.....					0.3522				5.42

TABLE XIII (*continued*).

No.	Amal at start.	Analysis of the equilibrium amalgam. K_2SO_4.	$SrSO_4$.	Hg.	Milli-equivs. of metals per 10 g. Hg.	Amalgamated metal fractions. K.	Sr.	Cc.	Cc. corr. to 0.1877 mg. equiv.
6.....	Sr	0.1106	0.2313	203.0	0.1866	0.5019	0.4981	2.64	2.66
7.....	Sr	0.1194	0.2336	204.3	0.1916	0.5187	0.4813	2.38	2.34
8.....	Sr	0.1118	0.2402	204.0	0.1912	0.4953	0.5047	2.74	2.68
9.....	K	0.1198	0.2293	215.8	0.1795	0.5242	0.4758	2.32	2.43
10.....	K	0.1083	0.2363	197.7	0.1930	0.4914	0.5086	2.81	2.73
11.....	K	0.1083	0.2267	201.4	0.1842	0.5018	0.4982	2.64	2.69
Mean.....					0.1877				2.59

From the data of Table XIV, and also from Fig. 4, it may be seen that, at a fixed amalgam concentration, C_c varies with the total salt concentra-

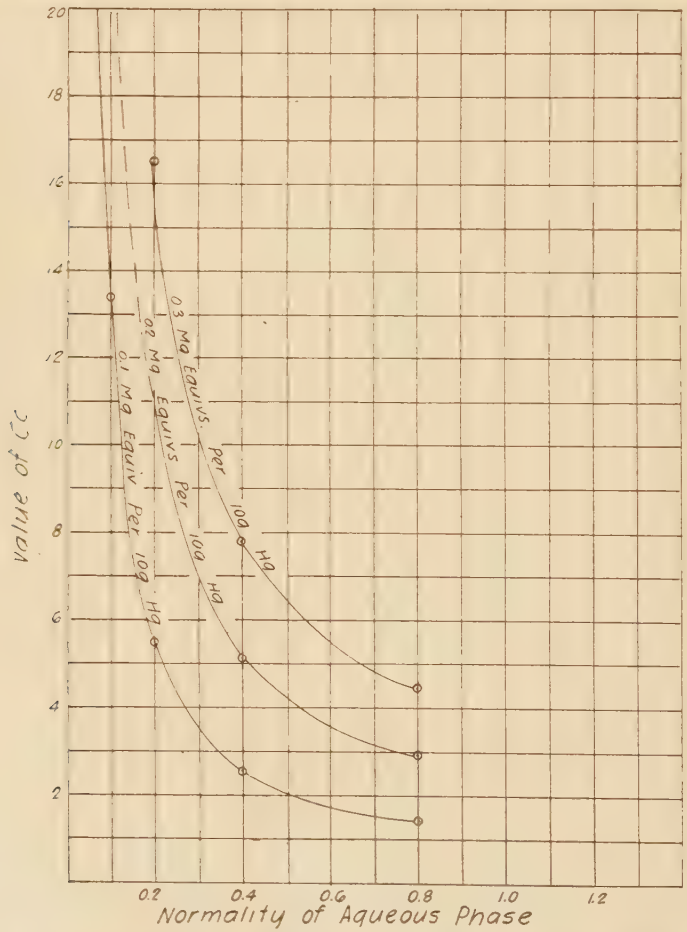

Fig. 4.—Showing value of C_c as a function of total salt concentration at various amalgam concentrations. Equivalent proportions of K and Sr in aqueous phase. Temp. 40°.

tion at 40° in a manner similar to that found at 25°. Assuming the heat effect to be constant over the temperature range studied, it is possible,

TABLE XIV.

Showing the Value of C_c as a Function of Total Salt Concentration at a Fixed (Equivalent) Salt-Concentration Ratio and at Various Specific Amalgam Concentrations at 40°.

Normality of aqueous phase.	0.1 mg. equiv. of metal per 10 g. Hg.	0.2 mg. equiv. of metal per 10 g. Hg.	0.3 mg. equiv. of metal per 10 g. Hg.
0.05	29.0	(63.0)	...
0.10	13.4	(25.9)	...
0.20	5.50	11.0	16.5
0.40	2.55	5.15	7.80
0.80	1.45	2.95	4.45

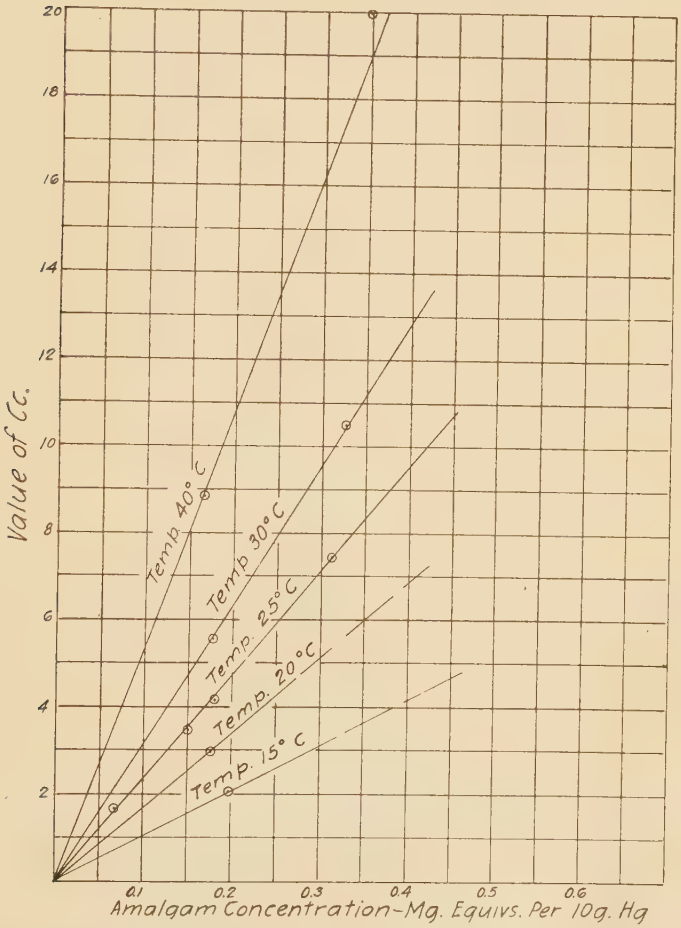

Fig. 5.—Showing value of C_c as a function of amalgam concentration at various temperatures. Equivalent proportions of K and Sr in aqueous phase. Total normality, 0.20.

by means of the van't Hoff equation, to calculate the heat of the interactions from the data obtained at these two temperatures. The heats of the interactions will be discussed in detail in a later section.

In the case of the aqueous solution of 0.2 N concentration, experiments were made at 15°, 20°, 25°, 30°, and 40°, in order to determine whether there is any appreciable difference in the heat effect within the temperature range studied. Tables XV, XVI and XVII, together with Tables III and XI, furnish the data necessary for this study. Table XVIII gives in summarized form the data at the different temperatures for specific amalgam concentrations, as read from Fig. 5. Fig. 6 shows the value of C_c as a function of temperature, for different fixed amalgam concentrations.

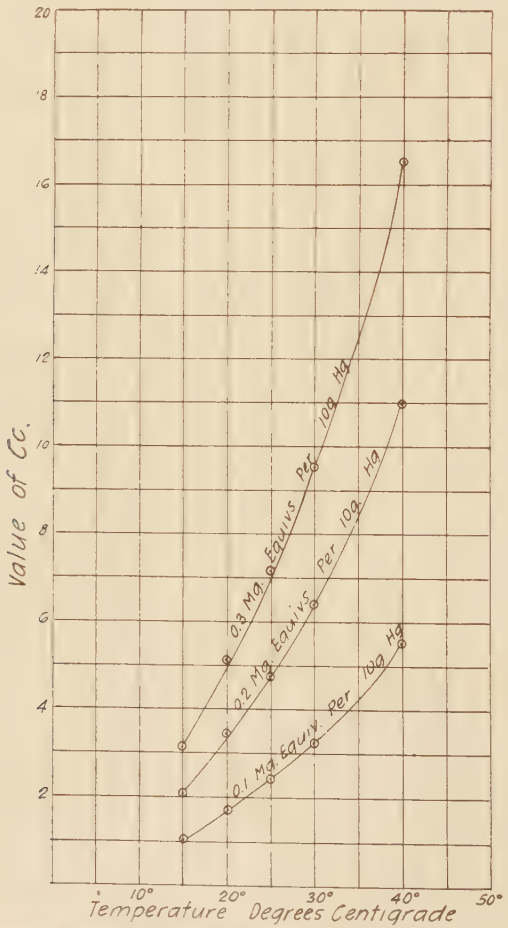

Fig. 6.—Showing value of C_c as a function of temperature at various amalgam concentrations. Equivalent proportions of K and Sr in aqueous phase. Total normality, 0.20.

TABLE XV.

Mixed Aqueous Phase 0.20 *N*. KCl : $\frac{1}{2}$ $SrCl_2$.

Temperature 30°.

No.	Amal. at start.	Analysis of the equilibrium amalgam. K_2SO_4.	$SrSO_4$.	Hg.	Milli-equivs. of metals per 10 g. Hg.	Amalgamated metal fractions. K.	Sr.	Cc.	Cc. corr. to 0.3257 mg. equiv.
1.....	Sr	0.0547	0.2970	104.9	0.3681	0.2802	0.7198	12.21	10.81
2.....	Sr	0.0531	0.2712	104.3	0.3414	0.2920	0.7080	11.06	10.50
3.....	Sr	0.0542	0.2765	103.8	0.3500	0.2921	0.7079	11.06	10.30
4.....	K	0.0496	0.2327	108.4	0.2864	0.3104	0.6896	9.54	10.82
5.....	K	0.0501	0.2393	103.9	0.3061	0.3064	0.6936	9.84	10.47
6.....	K	0.0500	0.2311	102.2	0.3023	0.3129	0.6871	9.35	10.08
Mean.....					0.3257				10.50
									Corr. to 0.1777.
7.....	Sr	0.0779	0.2539	204.1	0.1792	0.3931	0.6069	5.23	5.18
8.....	Sr	0.0776	0.2713	204.0	0.1884	0.3760	0.6240	5.87	5.53
9.....	Sr	0.0735	0.2387	204.6	0.1681	0.3938	0.6062	5.21	5.49
10.....	K	0.0808	0.2785	208.7	0.1898	0.3798	0.6202	5.73	5.37
11.....	K	0.0703	0.2388	208.8	0.1632	0.3833	0.6167	5.59	6.07
Mean.....					0.1777				5.53

TABLE XVI.

Temperature 20°.

									Corr. to 0.1744.
1.....	Sr	0.1062	0.2516	218.6	0.1812	0.4711	0.5289	3.17	3.05
2.....	Sr	0.1101	0.2732	209.4	0.2024	0.4593	0.5407	3.41	2.94
3.....	Sr	0.1050	0.2496	206.5	0.1898	0.4700	0.5300	3.20	2.94
4.....	K	0.1045	0.2323	209.9	0.1776	0.4867	0.5133	2.89	2.84
5.....	K	0.0972	0.1934	211.6	0.1522	0.5144	0.4856	2.45	2.81
6.....	K	0.0872	0.1796	206.1	0.1434	0.5055	0.4945	2.57	3.12
Mean.....					0.1744				2.95

TABLE XVII.

Temperature 15°.

									Corr. to 0.1964.
1.....	Sr	0.1325	0.2478	203.2	0.2077	0.5300	0.4700	2.24	2.12
2.....	Sr	0.1421	0.2679	209.6	0.2170	0.5279	0.4721	2.25	2.04
3.....	Sr	0.1495	0.3116	213.8	0.2390	0.5029	0.4971	2.61	2.14
4.....	K	0.1264	0.1940	206.6	0.1723	0.5787	0.4213	1.68	1.92
5.....	K	0.1198	0.1808	202.5	0.1651	0.5830	0.4170	1.59	1.89
6.....	K	0.1227	0.2055	205.5	0.1774	0.5575	0.4425	1.89	2.10
Mean.....					0.1964				2.04

TABLE XVIII.

Showing the Value of C_c as a Function of Temperature at a Fixed (Equivalent) Salt-Concentration Ratio but at Various Specific Amalgam Concentrations for a Total Salt Concentration of 0.20 *N*.

Temp.	0.1 mg. equiv. of metal per 10 g. Hg.	0.2 mg. equiv. of metal per 10 g. Hg.	0.3 mg. equiv. of metal per 10 g. Hg.
15°	1.05	2.10	(3.15)
20°	1.72	3.45	(5.10)
25°	2.40	4.75	7.15
30°	3.20	6.40	9.55
40°	5.50	11.00	16.55

4. Effect of Varying the Concentration Ratio of the Salts at a Fixed Normal Concentration and a Fixed Amalgam Concentration.—Tables XIXA, XIXB, XIXC, and XIXD; XXA, XXB, XXC, and XXD; and XXIA, XXIB, XXIC, and XXID contain the data obtained at total salt concentrations of 0.2 *N*, 0.4 *N*, and 0.8 *N*, respectively, upon varying the ratio of the salts. Solutions containing two and four equivalents of either salt

TABLE XIXA.

Mixed Aqueous Phase 0.20 *N*. 8 KCl : $SrCl_2$.

Temperature 25°.

No.	Amal. at start.	Analysis of the equilibrium amalgam. K_2SO_4.	$SrSO_4$.	Hg.	Milli-equivs. of metals per 10 g. Hg.	Amalgamated metal fractions. K.	Sr.	Cc.	Cc. corr. to 0.2781 mg. equiv.
1.....	Sr	0.1198	0.1422	103.1	0.2836	0.6400	0.3600	6.25	6.13
2.....	Sr	0.1237	0.1508	107.2	0.2855	0.6336	0.3664	6.49	6.33
3.....	Sr	0.1299	0.1749	103.5	0.3280	0.6103	0.3897	7.44	6.30
4.....	K	0.1095	0.1207	96.5	0.2667	0.6568	0.3432	5.66	5.92
5.....	K	0.1066	0.1165	100.7	0.2477	0.6587	0.3413	5.59	6.28
6.....	K	0.1051	0.1162	96.1	0.2572	0.6563	0.3437	5.67	6.12
Mean.....					0.2781				6.18
									Corr. to 0.1521.
7.....	Sr	0.1553	0.1152	200.5	0.1514	0.7399	0.2601	3.38	3.39
8.....	Sr	0.1614	0.1228	205.6	0.1553	0.7349	0.2651	3.49	3.41
9.....	Sr	0.1596	0.1196	201.1	0.1558	0.7379	0.2621	3.42	3.34
10.....	K	0.1592	0.1099	210.0	0.1441	0.7535	0.2465	3.09	3.26
11.....	K	0.1607	0.1155	206.4	0.1503	0.7457	0.2543	3.38	3.42
12.....	K	0.1587	0.1174	199.0	0.1557	0.7402	0.2598	3.37	3.29
Mean.....					0.1521				3.35

TABLE XIXB.

4 KCl : $SrCl_2$.

									Corr. to 0.2963.
1.....	Sr	0.0887	0.1910	101.9	0.3067	0.4947	0.5053	6.61	6.40
2.....	Sr	0.0886	0.2027	102.7	0.3143	0.4795	0.5205	7.24	6.83
3.....	Sr	0.0859	0.1971	100.1	0.3130	0.4792	0.5208	7.26	6.87
4.....	K	0.0850	0.1731	100.4	0.2851	0.5088	0.4912	6.07	6.32
5.....	K	0.0869	0.1824	105.9	0.2818	0.5011	0.4989	6.36	6.64
6.....	K	0.0843	0.1703	101.9	0.2767	0.5105	0.4895	6.01	6.44
Mean.....					0.2963				6.59
									Corr. to 0.1707.
7.....	Sr	0.1301	0.1994	202.4	0.1810	0.5791	0.4209	4.02	3.79
8.....	Sr	0.1377	0.2188	212.5	0.1865	0.5704	0.4296	4.23	3.87
9.....	Sr	0.1266	0.1847	204.7	0.1693	0.5909	0.4091	3.75	3.78
10.....	K	0.1224	0.1668	204.3	0.1575	0.6074	0.3926	3.40	3.69
11.....	K	0.1257	0.1725	203.8	0.1630	0.6056	0.3944	3.44	3.60
12.....	K	0.1302	0.1855	210.4	0.1671	0.5969	0.4031	3.62	3.70
Mean.....					0.1707				3.74

TABLE XIXc.

Mixed Aqueous Phase 0.20 *N*. KCl : $SrCl_2$.

Temperature 25°.

No.	Amal. at start.	Analysis of the equilibrium amalgam. K_2SO_4.	$SrSO_4$.	Hg.	Milli-equivs. of metals per 10 g. Hg.	Amalgamated metal fractions. K.	Sr.	Cc.	Cc. corr. to 0.1614 mg. equiv.
1.....	Sr	0.0484	0.2733	203.2	0.1737	0.2718	0.7282	4.92	4.58
2.....	Sr	0.0465	0.2630	205.2	0.1656	0.2719	0.7281	4.92	4.80
3.....	Sr	0.0476	0.2773	206.0	0.1731	0.2662	0.7338	5.18	4.83
4.....	K	0.0459	0.2503	203.9	0.1595	0.2787	0.7213	4.64	4.70
5.....	K	0.0456	0.2513	213.8	0.1524	0.2771	0.7229	4.71	4.98
6.....	K	0.0426	0.2227	202.4	0.1439	0.2872	0.7128	4.32	4.86
Mean.....					0.1614				4.79
									Corr. to 0.0923.
7.....	Sr	0.0677	0.2883	402.3	0.0973	0.3312	0.6688	3.05	2.90
8.....	Sr	0.0719	0.2795	409.5	0.0945	0.3519	0.6481	2.62	2.56
9.....	Sr	0.0858	0.4008	421.5	0.1269	0.3110	0.6890	3.56	2.60
10.....	K	0.0669	0.2492	409.5	0.0849	0.3613	0.6387	2.45	2.66
11.....	K	0.0590	0.2078	403.5	0.0729	0.3747	0.6253	2.23	2.83
12.....	K	0.0592	0.2257	406.5	0.0771	0.3565	0.6435	2.53	3.03
Mean.....					0.0923				2.76

TABLE XIXd.

KCl : $2SrCl_2$

									Corr. to 0.1788.
1.....	Sr	0.0541	0.6085	405.1	0.1789	0.1580	0.8420	5.62	5.62
2.....	Sr	0.0587	0.7952	420.3	0.2220	0.1350	0.8650	7.58	6.12
3.....	Sr	0.0528	0.6114	407.9	0.1781	0.1541	0.8459	5.94	5.98
4.....	K	0.0454	0.5659	410.2	0.1629	0.1448	0.8552	6.79	7.45
5.....	K	0.0463	0.5264	411.3	0.1522	0.1566	0.8434	5.73	6.73
Mean.....					0.1788				6.38
									Corr. to 0.0786.
6.....	Sr	0.0367	0.2656	396.3	0.0837	0.2259	0.7741	2.53	2.38
7.....	Sr	0.0304	0.2391	399.2	0.0740	0.2122	0.7878	2.91	3.09
8.....	Sr	0.0328	0.2802	397.2	0.0863	0.1978	0.8022	3.42	3.12
9.....	K	0.0317	0.2411	400.9	0.0746	0.2167	0.7833	2.78	2.93
10.....	K	0.0329	0.2417	393.3	0.0765	0.2234	0.7766	2.59	2.68
11.....	K	0.0325	0.2443	397.6	0.0763	0.2192	0.7808	2.71	2.79
Mean.....					0.0786				2.83

TABLE XXa.

Mixed Aqueous Phase 0.40 *N*. 8 KCl : $SrCl_2$.

Temperature 25°.

									Corr. to 0.3208.
1.....	Sr	0.1615	0.1282	103.2	0.3149	0.7267	0.2733	3.68	3.75
2.....	Sr	0.1616	0.1297	100.0	0.3267	0.7241	0.2759	3.74	3.68
3.....	Sr	0.1636	0.1363	100.7	0.3338	0.7167	0.2843	3.93	3.78
4.....	K	0.1600	0.1256	101.6	0.3153	0.7287	0.2713	3.63	3.70
5.....	K	0.1640	0.1214	107.8	0.2972	0.7401	0.2599	3.37	3.64
6.....	K	0.1765	0.1491	108.4	0.3367	0.7139	0.2861	3.99	3.80
Mean.....					0.3208				3.73

TABLE XXA (*continued*).

No.	Amal. at start.	Analysis of the equilibrium amalgam. K_2SO_4.	$SrSO_4$.	Hg.	Milli-equivs. of metals per 10 g. Hg.	Amalgamated metal fractions. K.	Sr.	Cc.	Cc. corr. to 0.1790 mg. equiv.
7.....	Sr	0.2180	0.1042	201.6	0.1805	0.8153	0.1847	1.98	1.96
8.....	Sr	0.2257	0.1150	204.9	0.1875	0.8055	0.1945	2.13	2.04
9.....	Sr	0.2178	0.1052	210.2	0.1735	0.8136	0.1864	2.00	2.06
10.....	K	0.2182	0.1011	206.2	0.1749	0.8199	0.1801	1.91	1.96
11.....	K	0.2215	0.1030	204.8	0.1788	0.8193	0.1807	1.92	1.92
Mean.....					0.1790				1.99

TABLE XXB.

4 KCl : $SrCl_2$.

									Corr. to 0.3035.
1.....	Sr	0.1230	0.1907	101.5	0.3435	0.5764	0.4236	4.06	3.62
2.....	Sr	0.1162	0.1620	101.8	0.3045	0.6031	0.3979	3.51	3.50
3.....	Sr	0.1204	0.1715	102.2	0.3178	0.5966	0.4034	3.63	3.48
4.....	K	0.1200	0.1578	105.9	0.2925	0.6159	0.3841	3.24	3.36
5.....	K	0.1126	0.1393	106.3	0.2641	0.6301	0.3699	2.98	3.43
6.....	K	0.1168	0.1605	103.4	0.2985	0.6055	0.3945	3.44	3.50
Mean.....					0.3035				3.48
									Corr. to 0.1595.
7.....	Sr	0.1651	0.1428	203.3	0.1696	0.7091	0.2909	1.85	1.74
8.....	Sr	0.1593	0.1416	201.5	0.1673	0.7036	0.2964	1.92	1.83
9.....	Sr	0.1685	0.1464	203.3	0.1735	0.7081	0.2919	1.86	1.71
10.....	K	0.1465	0.1082	203.7	0.1404	0.7407	0.2593	1.51	1.72
11.....	K	0.1522	0.1254	202.5	0.1537	0.7190	0.2810	1.74	1.80
12.....	K	0.1598	0.1253	210.1	0.1523	0.7287	0.2713	1.64	1.72
Mean.....					0.1595				1.75

TABLE XXC.

Mixed Aqueous Phase 0.40 *N*. KCl : $SrCl_2$.

Temperature 25°.

									Corr. to 0.1495.
1.....	Sr	0.0634	0.2271	202.6	0.1575	0.3709	0.6291	2.29	2.17
2.....	Sr	0.0593	0.2218	205.1	0.1510	0.3603	0.6397	2.46	2.43
3.....	Sr	0.0709	0.2489	202.8	0.1737	0.3751	0.6249	2.22	1.91
4.....	K	0.0636	0.2062	203.9	0.1459	0.3946	0.6054	1.95	2.00
5.....	K	0.0567	0.1930	207.0	0.1330	0.3831	0.6169	2.10	2.36
6.....	K	0.0600	0.1929	205.1	0.1359	0.3958	0.6042	1.93	2.12
Mean.....					0.1495				2.16
									Corr. to 0.0854.
7.....	Sr	0.0858	0.2279	393.7	0.0880	0.4424	0.5576	1.43	1.39
8.....	Sr	0.0993	0.2461	397.8	0.0961	0.4598	0.5402	1.28	1.14
9.....	Sr	0.0904	0.2203	401.6	0.0855	0.4640	0.5360	1.25	1.25
10.....	K	0.0857	0.2088	396.6	0.0821	0.4636	0.5364	1.25	1.30
11.....	K	0.0835	0.2057	396.2	0.0807	0.4614	0.5386	1.26	1.33
12.....	K	0.0854	0.1999	394.7	0.0799	0.4738	0.5262	1.17	1.25
Mean.....					0.0854				1.28

TABLE XXD.

KCl : $2SrCl_2$.

No.	Amal. at start.	Analysis of the equilibrium amalgam. K_2SO_4.	$SrSO_4$.	Hg.	Milli-equivs. of metals per 10 g. Hg.	Amalgamated metal fractions. K.	Sr.	Cc.	Cc. corr. to 0.1748 mg. equiv.
1.....	Sr	0.0418	0.3436	209.7	0.2013	0.2044	0.7956	3.17	2.75
2.....	Sr	0.0371	0.3336	204.1	0.1988	0.1904	0.8096	3.72	3.26
3.....	Sr	0.0344	0.2837	198.5	0.1754	0.2032	0.7968	3.22	3.21
4.....	K	0.0364	0.2578	212.2	0.1518	0.2291	0.7709	2.45	2.82
5.....	K	0.0332	0.2556	202.9	0.1560	0.2150	0.7850	2.83	3.17
6.....	K	0.0360	0.2739	204.9	0.1657	0.2175	0.7825	2.76	2.92
Mean.....					0.1748				3.02
									Corr. to 0.0807.
7.....	Sr	0.0534	0.2732	404.0	0.0888	0.2921	0.7079	1.38	1.25
8.....	Sr	0.0473	0.2558	400.7	0.0830	0.2802	0.7198	1.53	1.49
9.....	Sr	0.0493	0.2508	402.8	0.0818	0.2928	0.7072	1.37	1.35
10.....	K	0.0521	0.2421	409.3	0.0790	0.3122	0.6878	1.18	1.21
11.....	K	0.0457	0.2129	399.8	0.0710	0.3115	0.6885	1.18	1.34
12.....	K	0.0479	0.2503	407.8	0.0804	0.2874	0.7126	1.44	1.45
Mean.....					0.0807				1.35

TABLE XXIA.

Mixed Aqueous Phase 0.80 *N*. 8 KCl : $SrCl_2$.

Temperature 5°.

									Corr. to 0.3166.
1.....	Sr	0.2074	0.1025	105.8	0.3306	0.8101	0.1899	2.06	1.98
2.....	Sr	0.2043	0.1015	104.3	0.3308	0.8093	0.1907	2.07	1.99
3.....	Sr	0.2045	0.1067	105.5	0.3327	0.8016	0.1984	2.20	2.09
4.....	K	0.2041	0.0927	107.0	0.3133	0.8228	0.1772	1.86	1.88
5.....	K	0.1888	0.0899	103.5	0.3041	0.8158	0.1842	1.97	2.05
6.....	K	0.1892	0.0842	107.2	0.2881	0.8255	0.1745	1.82	2.00
Mean.....					0.3166				2.00
									Corr. to 0.1772.
7.....	Sr	0.2766	0.0843	207.8	0.1971	0.8738	0.1262	1.18	1.06
8.....	Sr	0.2672	0.0764	203.7	0.1913	0.8807	0.1193	1.09	1.01
9.....	Sr	0.2614	0.0796	206.4	0.1874	0.8737	0.1263	1.17	1.11
10.....	K	0.2344	0.0599	207.3	0.1613	0.8917	0.1083	0.97	1.06
11.....	K	0.2358	0.0608	201.6	0.1671	0.8911	0.1089	0.97	1.03
12.....	K	0.2210	0.0611	201.4	0.1590	0.8842	0.1158	1.05	1.17
Mean.....					0.1772				1.07

TABLE XXIB.

4 KCl : $SrCl_2$.

									Corr. to 0.2988.
1.....	Sr	0.1459	0.1438	98.5	0.3291	0.6814	0.3186	2.20	2.00
2.....	Sr	0.1457	0.1414	100.4	0.3199	0.6849	0.3151	2.15	2.01
3.....	Sr	0.1123	0.0790	101.2	0.2125	0.7479	0.2521	1.42	2.00
4.....	K	0.1528	0.1486	98.1	0.3438	0.6843	0.3157	2.16	1.88
5.....	K	0.1298	0.1201	94.5	0.2963	0.6951	0.3049	2.02	2.04
6.....	K	0.1392	0.1241	101.3	0.2912	0.7029	0.2971	1.93	1.98
Mean.....					0.2988				1.99

TABLE XXIB (*continued*).

No.	Amal. at start.	Analysis of the equilibrium amalgam. K_2SO_4.	$SrSO_4$.	Hg.	Milli-equivs. of metals per 10 g. Hg.	Amalgamated metal fractions. K.	Sr.	Cc.	Cc. corr. to 0.1831 mg. equiv.
7.....	Sr	0.2219	0.1403	203.0	0.2007	0.7694	0.2306	1.25	1.14
8.....	Sr	0.1991	0.1088	198.1	0.1750	0.7948	0.2052	1.04	1.09
9.....	Sr	0.2274	0.1355	202.2	0.2020	0.7797	0.2203	1.16	1.05
10.....	K	0.1862	0.1053	204.3	0.1608	0.7887	0.2113	1.08	1.23
11.....	K	0.2088	0.1092	207.1	0.1731	0.8012	0.1988	0.99	1.05
12.....	K	0.2183	0.1270	207.8	0.1872	0.7837	0.2163	1.13	1.10
Mean.....					0.1831				1.11

TABLE XXIC.

Mixed Aqueous Phase 0.80 *N*. $KCl : SrCl_2$.

Temperature 25°.

									Corr. to 0.3132.
1.....	Sr	0.0568	0.2057	105.8	0.2734	0.3680	0.6320	2.34	2.68
2.....	Sr	0.0596	0.2283	104.8	0.3026	0.3554	0.6446	2.56	2.65
3.....	Sr	0.0631	0.2769	103.4	0.3615	0.3243	0.6757	3.21	2.78
4.....	K	0.0564	0.2195	99.8	0.3043	0.3512	0.6488	2.63	2.70
5.....	K	0.0551	0.2334	97.8	0.3244	0.3321	0.6679	3.03	2.92
Mean.....					0.3132				2.75
									Corr. to 0.1817.
6.....	Sr	0.1004	0.2344	201.1	0.1843	0.4747	0.5253	1.17	1.15
7.....	Sr	0.0952	0.2448	205.6	0.1827	0.4505	0.5495	1.35	1.34
8.....	Sr	0.0937	0.2469	202.8	0.1856	0.4449	0.5551	1.40	1.37
9.....	K	0.0904	0.2427	214.3	0.1716	0.4402	0.5598	1.44	1.52
10.....	K	0.0945	0.2492	209.6	0.1801	0.4443	0.5557	1.41	1.42
11.....	K	0.0980	0.2438	203.7	0.1856	0.4588	0.5412	1.29	1.26
Mean.....					0.1817				1.34

TABLE XXID.

$KCl : 2\ SrCl_2$.

									Corr. to 0.3371.
1.....	Sr	0.0323	0.2769	100.3	0.3377	0.1974	0.8026	3.43	3.43
2.....	Sr	0.0319	0.2719	101.7	0.3272	0.1981	0.8019	3.41	3.52
3.....	K	0.0322	0.2936	109.5	0.3258	0.1883	0.8117	3.81	3.94
4.....	K	0.0328	0.2956	100.3	0.3584	0.1893	0.8107	3.77	3.54
Mean.....					0.3371				3.60
									Corr. to 0.2052.
5.....	Sr	0.0538	0.3591	207.6	0.2182	0.2404	0.7596	2.19	2.06
6.....	Sr	0.0511	0.3478	204.2	0.2142	0.2362	0.7638	2.28	2.19
7.....	Sr	0.0589	0.3370	208.7	0.2082	0.2691	0.7309	1.68	1.66
8.....	K	0.0491	0.3208	207.5	0.1954	0.2437	0.7563	2.12	2.22
9.....	K	0.0518	0.3021	205.2	0.1893	0.2659	0.7341	1.73	1.88
10.....	K	0.0540	0.3355	207.3	0.2061	0.2531	0.7469	1.94	1.93
Mean.....					0.2052				1.99

to one of the other were studied. Here also, as with equivalent salt mixtures, it is found that the value of C_c is a linear function of the amalgam concentration: Fig. 7 shows the results of this study, and Table XXII gives in summarized form the data, read from the plots in Fig. 7, showing the effect of changes in the salt-concentration ratio at a fixed normal concentration and at different fixed amalgam concentrations.

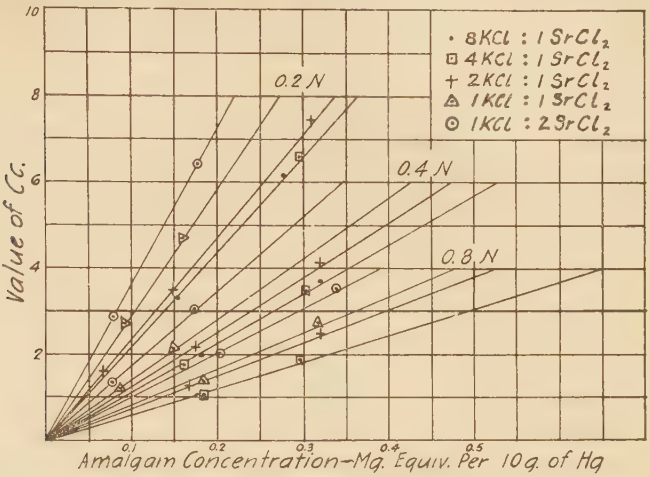

Fig. 7.—Showing C_c as a Function of Amalgam Concentration at Various Total Salt Concentrations and Varying Proportions of Potassium and Strontium in Aqueous Phase. Temp. 25° C.

TABLE XXII.

Showing the Value of C_c as a Function of the Change of Ratio of Salts at a Fixed Concentration and at Various Specific Amalgam Concentrations at 25°.

Normality of aqueous phase.	Ratio: equivs. K salt to equivs. Sr salt.	Value of C_c at amalgam conc. of: 0.1 mg. equiv. of metal per 10 g. Hg.	0.2 mg. equiv. of metal per 10 g. Hg.	0.3 mg. equiv. of metal per 10 g. Hg.
0.20	4:1	2.22	4.45	6.65
0.20	2:1	2.22	4.45	6.65
0.20	1:1	2.40	4.75	7.15
0.20	1:2	2.95	5.90	(8.80)
0.20	1:4	3.70	7.40	(10.95)
0.40	4:1	1.15	2.30	3.45
0.40	2:1	1.15	2.30	3.45
0.40	1:1	1.30	2.60	3.90
0.40	1:2	1.45	2.90	(4.35)
0.40	1:4	1.75	3.50	(5.25)
0.80	4.1	0.60	1.25	1.90
0.80	2:1	0.60	1.25	1.90
0.80	1:1	0.78	1.55	2.35
0.80	1:2	0.85	1.65	2.55
0.80	1:4	1.05	2.05	3.10

It will be noted that the values of C_c at any one specific amalgam concentration for any total salt concentration with a ratio of 4 equivalents of potassium salt to one of strontium salt are practically identical with the values of C_c obtained for the same total salt concentration but with a ratio of two equivalents of potassium salt to one equivalent of strontium salt. But as the proportion of strontium salt is further increased, the difference in value of C_c becomes more marked, the values obtained with a ratio of one equivalent of potassium salt to four equivalents of strontium salt being the greatest of all.

5. The Ion-Fraction Changes Which Take Place upon Increasing the Concentration of Aqueous Chloride Solutions of Potassium and Strontium Mixed in Equivalent Proportions.—It has been shown in the theoretical section that, given the value of C_o (Equation 4), the ion fractions of the metals in the individual aqueous mixtures may be calculated by means of the expression

$$(K^+) = \frac{-a + \sqrt{a^2 + 4a}}{2},$$

in which

$$a = \frac{C_o\,(\text{K-salt})^2}{C_c\,(\text{Sr-salt})}.$$

Table 8 contains the values of C_c for the different total salt concentrations, in the case of the equivalent mixtures; and, in order to make the ion-fraction calculations, it only remains to determine the value of C_o for some specific amalgam concentration. But, since we are in the dark concerning the respective degrees of dissociation of the strontium and potassium hydrargyrides in the mercurial phase, and also concerning the fractions of the simple (unhydrated) ions of strontium and potassium in the aqueous phase, there does not seem to be any good prospect for the determination of the C_o value. We are therefore compelled to start with some assumption concerning the value of C_o, the so-called "make-shift equilibrium constant," at a given amalgam concentration,[1] in order, with that as a basis, to study the ion-fraction changes which accompany changes in salt concentration in the aqueous phase. (Cf. also Section 8.)

If, as a starting point, we assume in the case of the most dilute salt

[1] Assuming the validity of Equations 2, 12, 13, and 14, C_o of Equation 4 is a make-shift equilibrium constant only in the sense that we use it as a stepping stone in the calculation of the fractions of the free, uncombined metal atoms and ions which enter into the real equilibrium expression (Equation 13).

From Equations 12 and 14, it follows that *the atomic concentrations of the uncombined strontium and potassium are directly proportional to the total atomic concentrations of the strontium and potassium (combined and uncombined), respectively, in the mercurial phase.* And, since, in the case of equilibria between individual amalgams of different concentration and identical aqueous phases (*i. e.*, aqueous phases in which the expression $(K^+)^2/(Sr^{++})$ has a constant, though unknown value), Equation 13 requires a con-

mixture studied that the value of n in Equation 6 is unity, we can then at least determine, by means of Equation 9, the direction and relative degree of the ion-fraction changes which accompany salt-concentration changes in the aqueous phase. Because the value of a in Equation 9 contains the factor C_o/C_c (Equation 7), and if, instead of this we employ the factor $C_{0.05}/C_c$, then, in place of a, we obtain in each case a

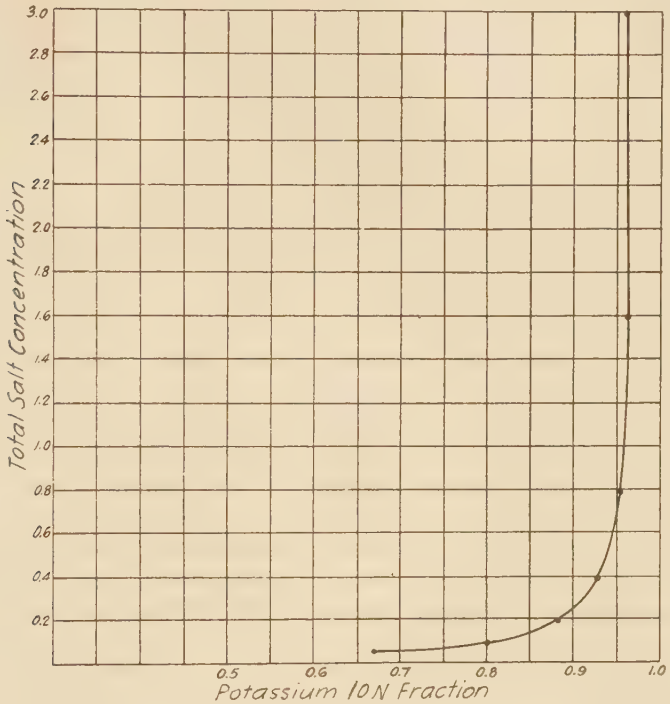

Fig. 8.—Showing ion fractions of potassium and strontium as a function of salt concentration in mixed equivalent aqueous solutions of the chlorides. Temp. 25°.

stant value also for $(Sr°_{Hg})/(K°_{Hg})^2$, it therefore follows that we should find identical numerical values for the expression

$$\frac{[Sr_{Hg}]}{[K_{Hg}]^2} \text{ or } \frac{\text{Milli-atoms of Sr per 100 g. of Hg}}{(\text{Milli-atoms of K per 100 g. of Hg})^2}.$$

The values of this expression in the cases of Expts. 5, 7, 15, 21, and 23 of Table III, the nearest approximations to the mean values of the individual runs at 5 different amalgam concentrations (6.2, 3.3, *2.07*, *1.6* and *0.8* milli-equivalents of metals per 100 g. of Hg), are 3.75, 3.01, *2.77*, *2.62* and *2.76*, respectively, and in the case of Expts. 1, 9, 16, 22, and 30 of Table IV (with 6.9, 5.5, 3.3, *1.8*, and *0.8* milli-equivalents of metals per 100 g. of Hg), the values are 1.84, 1.76, 1.53, *1.35* and *1.37*. In both instances, *i. e.*, with 0.2 *N* and 0.4 *N* aqueous phases, the results indicate in a very satisfactory manner that, within the experimental error, Equations 12 and 14 are valid in the case of the more dilute amalgam—up to about 2 milli-equivalents of the metals per 100 g. of mercury.

value which is proportional to a (= $C_{(x+y)}/(C_x \times a)$—so that the so-called ion fractions obtained in the individual cases on this basis all bear a fixed relationship to the actual ion-fraction values.

The ion fractions, at 25°, calculated on the basis just described, are given in Table XXIII, and in Fig. 8 these values are plotted against the total salt concentration. Although the two salts are present in equivalent proportions, the ion fraction of the potassium increases with the salt concentration, more and more slowly, until at about 1.6 *N* concentration it reaches a constant value. The same phenomenon was observed by Smith and Braley[1] in the case of aqueous chloride mixtures of sodium and strontium.

TABLE XXIII.

Showing the Ion-Fraction Changes Which Accompany Salt-Concentration Changes in Equivalent Aqueous Mixtures of Strontium and Potassium Chlorides at 25°.

Normality of mixed aqueous solution.	C_c value at x milli-equivs. of metals per 10 g. of mercury.[2]		Ion fraction, calculated on the assumption that, in 0.05 *N* equivalent mixture, a (Equation 6) = 1.			
			$x = 0.1$.		$x = 0.2$.	
	$x = 0.1$.	$x = 0.2$.	(K^+).	(Sr^{++}).	(K^+).	(Sr^{++}).
0.05	11.7	(23.0)	*0.6666*	*0.3333*	*0.6666*	*0.3333*
0.1	5.05	9.95	0.805	0.195	0.797	0.203
0.2	2.40	4.75	0.881	0.119	0.882	0.118
0.4	1.30	2.60	0.928	0.072	0.928	0.072
0.8	0.78	1.55	0.954	0.046	0.955	0.045
1.6	0.62	1.28	0.963	0.037	0.962	0.038
3.0	0.65	1.35	0.961	0.039	0.960	0.040

TABLE XXIV.

Showing the Ion-Fraction Changes Which Accompany Salt-Concentration Changes in Equivalent Aqueous Mixtures of Strontium and Potassium Chlorides at 40°.

0.05	29.0	(63.0)	*0.6666*	*0.3333*	*0.6666*	*0.3333*
0.1	13.4	25.9	0.786	0.214	0.802	0.198
0.2	5.5	11.0	0.888	0.112	0.895	0.105
0.4	2.55	5.15	0.942	0.058	0.945	0.055
0.8	1.45	2.95	0.965	0.035	0.967	0.033

6. **Effect of the Temperature upon the Ion-Fraction Changes in Aqueous Chloride Solutions Mixed in Equivalent Proportions.**—Table XIV contains the C_x values obtained at 40°, at amalgam concentrations of 0.1 and 0.2 milli-equivalents of metals per 10 g. of mercury. The concentration range studied in this case was from 0.05 *N* to 0.8 *N*. The calculated ion fractions will be found in Table XXIV. The general behavior is very similar to that at 25°. At either temperature, it will be noted that practically identical results are obtained, whether the calculations are based upon an amalgam concentration of 0.1 or 0.2 milli-equivalents of metals per 10 g. of mercury.

[1] *Loc. cit.*

[2] The C_x values in Table XXIII are taken from Table VIII, and those in Table XXIV are taken from Table XIV.

7. Ionic Changes Produced in Mixed Chloride Solutions of Strontium and Potassium upon Varying the Salt-Concentration Ratio.—It has already been shown that the value of C_o must remain constant, regardless of the ratio of salts in the aqueous phase, provided the total equivalent concentration of the mercurial phase is kept constant. If, therefore, as a point of departure, we again use the C_c value obtained at 25° with the equivalent aqueous mixture of 0.05 N concentration, at an amalgam concentration of 0.1 milli-equivalent of metals per 10 g. of mercury, we may calculate the ion fractions on the same basis as before, and study the effect of varying the salt-concentration ratio at various normal concentrations of the aqueous phase. (Cf. also Section 8, Table XXX.)

Table XXV contains the results of these calculations, and in Table XXVI are given the ion-fraction ratios $(K^+)/(Sr^{++})$ along with the mol-fraction ratios $(KCl)/(SrCl_2)$ of the salts. It will be seen that the ion fraction of the potassium is greatly in excess of the mol fraction of potassium chloride which supplies the ion; also that this excess is greatly increased either by increasing the normal concentration of the solution at a fixed salt ratio, or by increasing the potassium salt fraction at a fixed normal concentration; it is especially increased by increasing both the potassium salt fraction and the normal concentration.

In Fig. 9, the mol fractions in which the salts are present in the mixtures are plotted against the corresponding ion fractions, and it is apparent that the latter are by no means proportional to the former. If they were proportional, these ratios would be identical, and the curve would be a straight line cutting the plot diagonally as shown by the broken line. The fact that at a specific total salt concentration the ion fractions are not proportional to the mol fractions in the solutions is a point which has been used to prove that the mass law does not hold for concentrated solutions of the strong electrolytes. In this investigation, however, an application of the mass law itself shows that the simple ion fractions of the metals are not proportional to the mol fractions of the salts in the solutions; that is, *the use of the mass law leads to the very conclusion that has been used*

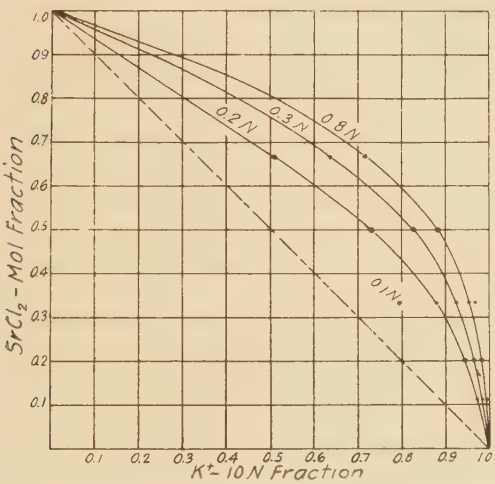

Fig. 9.—Showing the relationship between the simple ion fractions of the metals and the mol fractions of the salts in the solutions. Temp. 25°.

against it.[1] Perhaps we should be more successful in applying the mass law to such solutions if we were better acquainted with the various molecular species which they contain.

TABLE XXV.

Showing the Ion-Fraction Differences in Mixed Chloride Solutions of Strontium and Potassium at Different Salt-Concentration Ratios and at Various Total Salt Concentrations. Temperature 25°.

Normality of mixed aqueous phase.	Mol fractions of salts. (KCl).	(SrCl₂).	C_c value at 0.1 milli-equiv. conc.[2]	Calculated ion fractions. (K^+).	(Sr^{++}).
0.05	0.6666	0.3333	11.7	*0.6666*	*0.3333*
0.2	0.8888	0.1111	2.22	0.975	0.025
0.2	0.8000	0.2000	2.22	0.947	0.053
0.2	0.6666	0.3333	2.40	0.881	0.119
0.2	0.5000	0.5000	2.95	0.731	0.269
0.2	0.3333	0.6666	3.70	0.509	0.491
0.4	0.8888	0.1111	1.15	0.987	0.013
0.4	0.8000	0.2000	1.15	0.970	0.030
0.4	0.6666	0.3333	1.30	0.928	0.072
0.4	0.5000	0.5000	1.45	0.829	0.171
0.4	0.3333	0.6666	1.75	0.636	0.364
0.8	0.8888	0.1111	0.60	0.992	0.008
0.8	0.8000	0.2000	0.60	0.983	0.017
0.8	0.6666	0.3333	0.78	0.954	0.046
0.8	0.5000	0.5000	0.85	0.886	0.114
0.8	0.3333	0.6666	1.05	0.720	0.280

TABLE XXVI.

Comparison of the Salt Mol-Fraction Ratio with the Metal Ion-Fraction Ratio in the Mixed Chloride Solutions, at 25°.

Normal concentration of the mixed solution.	Mol-fraction ratio of the salts: (KCl)/($SrCl_2$).	Ion-fraction ratio of the metals: (K^+)/(Sr^{++}).
0.2	8	39.0
0.2	4	17.9
0.2	2	7.40
0.2	1	2.72
0.2	0.5	1.04
0.4	8	75.9
0.4	4	32.3
0.4	2	12.9
0.4	1	4.84
0.4	0.5	1.73
0.8	8	124.0
0.8	4	57.8
0.8	2	20.7
0.8	1	7.77
0.8	0.5	2.59

[1] This same fact was previously observed in the case of the sodium-strontium equilibrium. Cf. Smith and Braley, *Loc. cit.*, p. 1571 (1917); p. 197 (1918).

[2] These C_c values are taken from Tables VIII and XXII.

8. The Mass Law and the Constitution of the Mercurial Phase.—If Equations 12 and 14 are valid, then it follows that the respective *concentrations* of the uncombined atoms of strontium and potassium are directly proportional to the total atomic concentrations of the strontium and potassium (combined and uncombined) in the mercurial phase. And since, in the case of equilibria between individual amalgams of different concentration and identical aqueous phases (*i. e.*, aqueous phases in which the expression $(K^+)^2/(Sr^{++})$ has a constant, though unknown value), Equation 13 requires a constant value also for $(Sr^o_{Hg})/(K^o_{Hg})^2$, it therefore follows that with the different dilute equilibrium amalgams we should find identical numerical values for the expression

$$\frac{[Sr_{Hg}]}{[K_{Hg}]^2},$$

in which $[Sr_{Hg}]$ and $[K_{Hg}]$ are the total atomic *concentrations*[1] of strontium and potassium, combined and uncombined, in the mercurial phase.

The values of this expression in the cases of two series of amalgams, in equilibrium with equivalent salt mixtures of 0.2 *N* and of 0.4 *N* concentration, are given in the last column of Table XXVII and of Table XXVIII, respectively, in the order of decreasing amalgam concentration. In both instances, *i. e.*, with 0.2 *N* and with 0.4 *N* identical aqueous phases, the results indicate in a very satisfactory manner that, within the experimental error, Equations 12 and 14 are valid in the case of the more dilute amalgams—up to about 2 milli-equivalents of the metals per 100 g. of mercury. In Table XXIX are given the values, for amalgam concentrations ranging from 3.435 to 1.404 milli-equivalents per 100 g. of mercury, and for an aqueous phase of 0.4 *N* concentration containing two equivalents of potassium chloride to one equivalent of strontium chloride. In this case, also, a constant value is reached at an amalgam concentration of about 2 milli-equivalents of metals per 100 g. of mercury.

Assuming that the hydrargyrides of strontium and potassium are dissociated slightly in mercurial solution according to Equation 1, these results show clearly that in the more dilute amalgams the total-atomic concentration expression $[Sr_{Hg}]/[K_{Hg}]^2$ is proportional to the uncombined atomic concentration expression $[Sr^o_{Hg}]/[K^o_{Hg}]^2$, from which, on the basis of Equation 2, it follows that

$$\frac{[Sr_{Hg}]\,[K^+]^2}{[K_{Hg}]^2\,[Sr^{++}]} = k. \qquad (15)$$

Since we are in ignorance concerning the concentrations of the simple metallic ions, we are compelled to start with an assumption concerning the values of the ion fractions (K^+) and (Sr^{++}) in the case of some par-

[1] It may again be mentioned that atomic fractions are denoted by parentheses, while actual concentrations are indicated by means of square brackets.

ticular mixed salt solution, in order, with that as a basis, to study the uncombined atom-fraction changes and the ion-fraction changes which accompany changes in salt concentration in the aqueous phase. Assuming, as in Sections 5 and 7, that in the case of the 0.05 N equivalent mixture of the chlorides $(K^+) = 0.6666$ and $(Sr^{++}) = 0.3333$, we obtain (Table XXX):

$$k = 14.33 \frac{0.6666^2}{0.3333} = 19.10$$

TABLE XXVII.

Mixed Aqueous Phase 0.2 N. KCl : $\frac{1}{2}$ $SrCl_2$.

No. of expt. in Table III.	Milli-equivs. per 10 g. Hg.	Amalg. metal fractions. (K_{Hg}).	Amalg. metal fractions. (Sr_{Hg}).	Actual milli-atoms per 100 g. Hg. $[K_{Hg}]$.	Actual milli-atoms per 100 g. Hg. $[Sr_{Hg}]$.	$[Sr_{Hg}]/[K_{Hg}]^2$.
5	0.6213	0.2396	0.7604	0.846	2.684	3.75
8	0.3758	0.3154	0.6846	0.703	1.527	3.11
7	0.3303	0.3342	0.6658	0.663	1.320	3.01
11	0.2879	0.3591	0.6409	0.630	1.125	2.83
10	0.2525	0.3685	0.6315	0.564	0.981	3.03
15	0.2070	0.4059	0.5941	0.527	0.771	*2.78*
13	0.1914	0.4188	0.5812	0.507	0.703	*2.73*
17	0.1800	0.4285	0.5715	0.491	0.654	*2.72*
16	0.1685	0.4360	0.5640	0.469	0.608	*2.82*
21	0.1596	0.4515	0.5485	0.465	0.565	*2.61*
23	0.0829	0.5408	0.4592	0.307	0.261	*2.77*
25	0.0614	0.6095	0.3905	0.254	0.180	*2.79*
26	0.0526	0.6107	0.3893	0.231	0.147	*2.76*
				(Mean of last eight = 2.75)		

TABLE XXVIII.

Mixed Aqueous Phase 0.4 N. KCl : $\frac{1}{2}$ $SrCl_2$.

No. of expt. in Table IV.	Milli-equivs. per 10 g. Hg.	Amalg. metal fractions. (K_{Hg}).	Amalg. metal fractions. (Sr_{Hg}).	Actual milli-atoms per 100 g. Hg. $[K_{Hg}]$.	Actual milli-atoms per 100 g. Hg. $[Sr_{Hg}]$.	$[Sr_{Hg}]/[K_{Hg}]^2$.
1	0.6859	0.3083	0.6917	1.250	2.804	1.84
9	0.5511	0.3372	0.6628	1.118	2.196	1.76
7	0.4449	0.3685	0.6315	1.005	1.722	1.70
16	0.3332	0.4225	0.5775	0.892	1.220	1.53
19	0.2843	0.4468	0.5532	0.818	1.012	1.51
12	0.2655	0.4547	0.5453	0.781	0.937	1.53
20	0.2176	0.5008	0.4992	0.727	0.724	*1.37*
21	0.1852	0.5272	0.4728	0.663	0.595	*1.35*
22	0.1785	0.5327	0.4673	0.648	0.568	*1.35*
24	0.1455	0.5568	0.4432	0.561	0.447	*1.42*
23	0.1384	0.5586	0.4414	0.536	0.424	*1.47*
26	0.1097	0.5980	0.4020	0.468	0.314	*1.37*
25	0.0931	0.6211	0.3789	0.419	0.256	*1.45*
30	0.0803	0.6501	0.3499	0.387	0.208	*1.39*
29	0.0784	0.6471	0.3529	0.375	0.204	*1.45*
28	0.0732	0.6595	0.3405	0.360	0.186	*1.44*
				(Mean of last ten = 1.37)		

And with this provisional value of k as a basis, setting $(K^+) = x$ and $(Sr^{++}) = 1 - x$, we are in a position on the same basis as before to solve Equation 15 for the value of (K^+) in the case of each individual aqueous phase, and therefore that of (K^o_{Hg}) in the mercurial phase. This has been done in the case of the 0.4 N salt mixtures and the values (essentially identical with those previously obtained) are given in the last column of Table XXX.

TABLE XXIX.

Mixed Aqueous Phase 0.4 N. 2 KCl : $^1/_2$ $SrCl_2$.

No. of expt. in Table XXB.	Milli-equivs. per 10 g. Hg.	Amalg. metal fractions. (K_{Hg}).	Amalg. metal fractions. (Sr_{Hg}).	Actual milli-atoms per 100 g Hg. $[K_{Hg}]$.	Actual milli-atoms per 100 g Hg. $[Sr_{Hg}]$.	$[Sr_{Hg}]/[K_{Hg}]^2$.
1	0.3435	0.5764	0.4236	1.390	1.022	0.529
3	0.3178	0.5966	0.4034	1.351	0.913	0.500
4	0.2925	0.6159	0.3841	1.301	0.812	0.486
5	0.2641	0.6301	0.3699	1.214	0.713	0.484
9	0.1735	0.7081	0.2919	0.951	0.392	*0.433*
7	0.1696	0.7091	0.2909	0.931	0.382	*0.441*
12	0.1523	0.7287	0.2713	0.873	0.325	*0.426*
10	0.1404	0.7407	0.2593	0.826	0.299	*0.438*

(Mean of last four = 0.434)

TABLE XXX.

Mixed Aqueous Phase 0.4 N. Varying Salt Proportions.

No. of table containing original data.	Mean of expts. No.	Molal conc. of salts. [KCl].	Molal conc. of salts. $[SrCl_2]$.	Milli-equivs. of metals per 10 g. Hg.	Actual milli-atoms per 100 g. Hg. $[K_{Hg}]$.	Actual milli-atoms per 100 g. Hg. $[Sr_{Hg}]$.	$\frac{[Sr_{Hg}]}{[K_{Hg}]^2}$	Calc. ion fraction (K^+).[1]
I	1-12	0.0250	0.0125	0.0684	0.138	0.273	14.33	*0.6666*
XXA	7-11	0.3200	0.0400	0.1790	1.230	0.280	0.185	0.987
XXB	7-12	0.2666	0.0666	0.1595	0.893	0.351	0.440	0.978
IV	25-30	0.2000	0.1000	0.0881	0.410	0.235	1.398	0.936
XXC	7-12	0.1333	0.1333	0.0854	0.256	0.299	4.56	0.834
XXD	7-12	0.0800	0.1600	0.0807	0.140	0.333	17.01	0.638

9. Heats of the Interactions.—In Table XXXI are given the values of $\frac{[Sr_{Hg}]\,[KCl]^2}{[K_{Hg}]^2[SrCl_2]} = k_s$, in the case of interactions between amalgams and 0.05 N, 0.10 N, 0.20 N, 0.40 N, 0.80 N, and 1.60 N mixed salt solutions, for various temperatures. The heat of the interaction

$$2K_{Hg} + SrCl_{2Aq} \rightleftarrows 2KCl_{Aq} + Sr_{Hg}$$

may now be calculated, in the case of each aqueous solution, from the values of k_s at different temperatures, by means of the van't Hoff equation

$$2.303 \log_{10} \frac{k_{s_2}}{k_{s_1}} = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

[1] The values of (K^+) previously found in the case of the 0.4 N aqueous mixtures (Table XXV) are 0.987, 0.970, 0.928, 0.829, and 0.636. Table XXX is introduced at this place mainly to show that the previous calculations, in which fractional concentrations alone were used, are reliable, even in the case of mixtures containing the salts in varying proportions.

in which k_{s_2} and k_{s_1} are the equilibrium values in the case of identical salt mixtures at the absolute temperatures T_2 and T_1, respectively, R the gas constant in calories (1.9852), and Q the heat evolved when the above reaction proceeds from right to left.

The heats of the individual interactions are given in Table XXXII. The reactions as represented are, as a whole, exothermic. As determined, these heats are the algebraic sum of the heats of several actions—dilution and ionization of salts, dissociation of complexes, etc.—and, individually, they are of significance mainly with respect to the order of magnitude and direction. A comparative study, however, of the heats of the different interactions leads to some definite ideas concerning the heats of dilution of the (dilute) amalgams and of the mixed salt solutions.

Since in the case of the interaction between any one solution and different amalgams the value of k_s remains constant at a specific temperature (cf. the data in Table XXXI, from Tables II, III, and IV), it is seen that in the case of sufficiently dilute amalgams the heat is not affected by the amalgam concentration. In other words, the heat of dilution of the mixed amalgams of a concentration below 0.2 milli-equivalents of metals per 10 g. of mercury is practically equal to zero. This behavior is in good agreement with Equations 12 and 14.

TABLE XXXI.

Table contg. original data.	Mean of expts.	Temp.	Molal conc. of salts. [KCl].	Molal conc. of salts. [$SrCl_2$].	Milli-equivs. per 10 g. Hg.	Actual mg. atoms per 100 g. Hg. [K_{Hg}].	Actual mg. atoms per 100 g. Hg. [Sr_{Hg}].	$\frac{[Sr_{Hg}][KCl]^2}{[K_{Hg}]^2[SrCl_2]}=k_s$.	
I	1–12	25	0.0250	0.0125	0.0684	0.138	0.273	0.717	
IX	1–11	40	0.0250	0.0125	0.0742	0.093	0.325	1.877	
II	1– 6	25	0.0500	0.0250	0.1401	0.300	0.550	0.611	0.604
	7–12	25	0.0500	0.0250	0.0743	0.211	0.266	0.597	
X	1– 6	40	0.0500	0.0250	0.0814	0.139	0.338	1.759	
XVII	1– 6	15	0.1000	0.0500	0.1964	0.739	0.613	0.225	
XVI	1– 6	20	0.1000	0.0500	0.1744	0.558	0.593	0.382	
III	13–18	25	0.1000	0.0500	0.1805	0.491	0.657	0.545	
	19–21	25	0.1000	0.0500	0.1511	0.450	0.530	0.523	0.528
	22–26	25	0.1000	0.0500	0.0676	0.278	0.199	0.515	
XV	7–11	30	0.1000	0.0500	0.1777	0.435	0.671	0.710	
XI	7–12	40	0.1000	0.0500	0.1642	0.314	0.664	1.347	
IV	20–24	25	0.2000	0.1000	0.1730	0.632	0.549	0.550	0.555
	25–30	25	0.2000	0.1000	0.0881	0.410	0.235	0.559	
XII	6–10	40	0.2000	0.1000	0.1772	0.468	0.652	1.193	
V	12–16	25	0.4000	0.2000	0.1678	0.759	0.459	0.637	
XIII	6–11	40	0.4000	0.2000	0.1877	0.635	0.621	1.232	
VI	1– 5	25	0.8000	0.4000	0.1729	0.782	0.473	1.237	

In the case of the 0.2 N equivalent mixtures, the data for the different temperature intervals show that Q is not strictly constant, though the main variation does not lie between 25° and 40°.

TABLE XXXII.

Showing the Heats of the Interactions.

0.2 *N* Equivalent Salt Mixture.

Temp. interval.	15–20°.	20–25°.	25–30°.	30–40°.	
Calories evolved.....	17745	11225	10620	12060	..

Temp. Interval 25–40°: Increasing Concentration.

Normality of equivalent salt mixture.	0.05 *N*.	0.10 *N*.	0.20 *N*.	0.40 *N*.	0.80 *N*.
Calories evolved.....	12800	13100	11560	9450	8140

The effect of changing the temperature upon the value of C_c, in the case of the 0.2 *N* salt mixture, has been shown in Fig. 6. The effect of changing the temperature upon the value of k_s, in the case of the same salt mixture, is shown in Fig. 10. As was to be expected, the two curves are of the same general appearance.

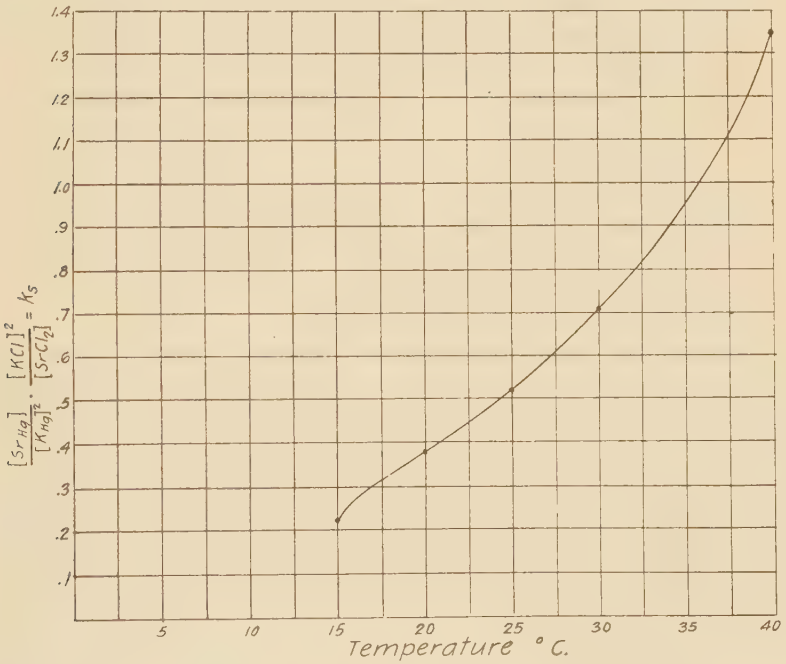

Fig. 10.—Showing k as a function of temperature in the case of an equivalent salt mixture of 0.2 *N* concentration.

The value of C_c as a function of total salt concentration in the case of equivalent mixtures at 25° has been shown in Fig. 2; and the value of k_s as a function of salt concentration for the same solutions at 25° is shown in Fig. 11. These curves are very unlike one another, in consequence of the fact that the values of $(KCl)^2/(SrCl_2)$ are identical in all cases, while those of $[KCl]^2/[SrCl_2]$ vary with the salt concentration.

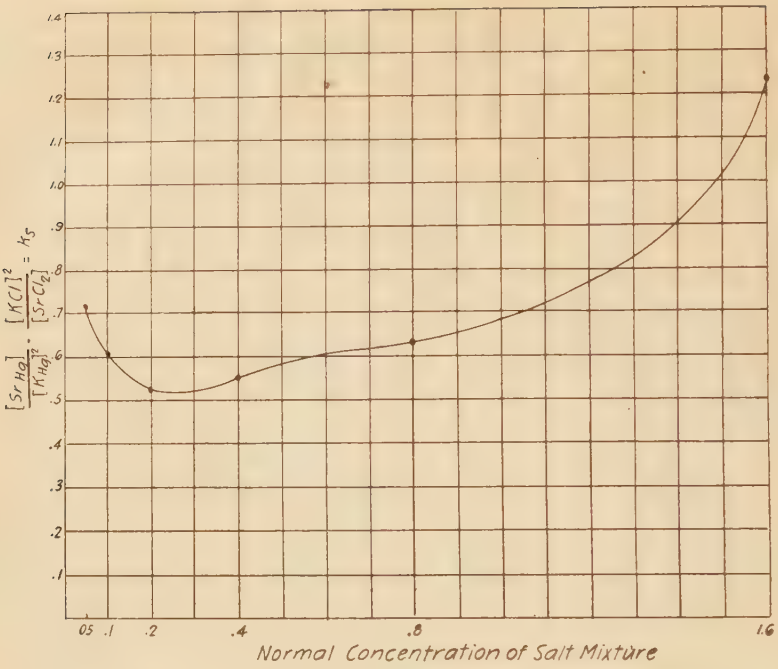

Fig. 11.—Showing k as a function of salt concentration in the case of equivalent mixtures at 25°.

E. Discussion.

This investigation has shown that in equivalent mixtures of potassium and strontium chlorides, the simple strontium-ion fraction (Sr^{++}) decreases, while the simple potassium-ion fraction (K^{+}) correspondingly increases, with increasing total salt concentration.

Kendall[1] has quite recently emphasized the ideas of Werner in regard to the mechanism of the ionization process. "Ionization is preceded by combination between solvent and solute and is, indeed, a consequence of such combination and the two phenomena proceed in parallel."

The formation of higher-order compounds between solvent and solute, with subsequent interpolation by the solvent, may occur to different extents, and the dissociation of these interpolated compounds is capable of furnishing ions of many different species. This is especially true in the case of mixed salt solutions, in which not only the solvent and a salt but also the two salts may take part in the formation of the higher-order complexes.

Briefly, the ionization of strontium chloride and of potassium chloride

[1] *J. Am. Chem. Soc.*, **39**, 2323 (1917); cf. G. McP. Smith, *Ibid.*, **35**, 39 (1913); Smith and Ball, *Loc. cit.*, and Smith and Braley, *Ibid.*

may be considered to be a consequence of reactions between solvent and solute of the following nature:

$$\begin{bmatrix} Cl \\ Sr \\ Cl \end{bmatrix} + nH_2O \rightleftarrows \begin{bmatrix} (H_2O)_m \\ Sr \\ Cl_2 \end{bmatrix} + (n - m)H_2O \quad (16)$$

$$\begin{bmatrix} (H_2O)_m \\ Sr \\ Cl_2 \end{bmatrix} + H_2O \rightleftarrows \begin{bmatrix} (H_2O)_{m+1} \\ Sr \\ Cl \end{bmatrix} Cl \quad (17)$$

$$\begin{bmatrix} (H_2O)_{m+1} \\ Sr \\ Cl \end{bmatrix} Cl + H_2O \rightleftarrows \begin{bmatrix} Sr(H_2O)_{m+2} \end{bmatrix} Cl_2 \quad (18)$$

and $$[KCl] + nH_2O \rightleftarrows [K(H_2O)_n]Cl \quad (19)$$

In the case of mixed solutions of these salts, molecules of either salt may also take part in the formation of higher-order compounds, *e. g.*,

$$\begin{bmatrix} (H_2O)_m \\ Sr \\ Cl_2 \end{bmatrix} + KCl \rightleftarrows \begin{bmatrix} (H_2O)_{m-1} \\ Sr \\ Cl_3 \end{bmatrix} K + H_2O \quad (20)$$

$$\begin{bmatrix} (H_2O)_{m-1} \\ Sr \\ Cl_3 \end{bmatrix} K + KCl \rightleftarrows \begin{bmatrix} (H_2O)_{m-2} \\ Sr \\ Cl_4 \end{bmatrix} K_2 + H_2O \quad (21)$$

and $$\begin{bmatrix} (H_2O)_{n-1} \\ K \\ Cl \end{bmatrix} + SrCl_2 = \begin{bmatrix} (H_2O)_{n-2} \\ K \\ Cl_2 \end{bmatrix} (SrCl) + H_2O \quad (22)$$

Disregarding the neutral water molecules, then, such high-order compounds would yield upon ionization ions such as $SrCl^+$, $SrCl_3^-$, $SrCl_4^{--}$, KCl_2^-, etc. Noyes and Falk,[1] in consequence of a study of transference numbers in relation to the properties of salt solutions, have referred to the probable existence of complex ions such as $BaCl_4^{--}$.

The relative extent of the formation of these higher-order compounds with the different metallic elements as centers, or the relative degree of stability of the complexes with the different metallic nuclei, largely determines whether there will exist in the mixture a preponderance of the ionic species consisting of simple singly charged potassium atoms or of simple doubly charged strontium atoms.

The results of this investigation are entirely in harmony with the existence of such ions as those predicted by Werner. The probability of the preponderance of complex ions derived from the higher-order compounds of strontium chloride rather than from those of potassium chloride would account for the relatively low Sr^{++}-ion concentration as compared with

[1] *J. Am. Chem. Soc.*, **33**, 1455 (1911).

the K^+-ion concentration in the more concentrated mixtures of the two salts.

In 1911, Harkins advocated the application of the intermediate-ion hypothesis to salts, as well as to polybasic acids; and, in a series of investigations on the effect of salts on the solubility of other salts, evidence has been furnished which would seem to show that the existence of such ions in solutions of uni-bivalent and bi-univalent salts can no longer be questioned seriously. In one of these investigations,[1] the effect of potassium chloride upon the solubility of strontium chloride was studied. Although attention is called to the fact that, in the case of a salt as soluble as strontium chloride, the effect might be masked by the specific solubility of the strontium chloride, the solubility was nevertheless found to be notably affected by the addition of potassium chloride. According to Harkins, the first step in the ionization of strontium chloride is

$$SrClCl \rightleftarrows SrCl^- + Cl^-,$$

and in very concentrated solutions this should be almost the only form of ionization. In the more dilute solutions the $SrCl^-$ will ionize to give the simple Sr^{++} ion

$$SrCl^+ \rightleftarrows Sr^{++} + Cl^-.$$

In the case of potassium chloride, only one form of simple ionization would be possible

$$KCl \rightleftarrows K^+ + Cl^-.$$

Upon mixing solutions of these two salts, mass-action considerations would lead us to expect the common Cl^- ion to force back the ionization of the intermediate $SrCl^+$ ion.

These conceptions are also in accord with the results of the present investigation; but attention should be called to the fact that such conceptions of ionization are by no means as recent as 1911; they were advanced long before by A. Werner. The intermediate $SrCl^-$ ion is nothing more than one of the ionic species resulting from the ionization of the interpolation compound represented in Equation 17 (or in Equation 22), with the molecules of water omitted; and, furthermore, this ion represents only one of the numerous types of ions that may result from the dissociation of the higher-order compounds in such systems. In the concentrated solutions of strontium chloride, the first ionization is in preponderance probably because the mass proportions of water are insufficient to force the interpolation further. It has been well proven that the ions are hydrated in aqueous solution; the existence of higher-order compounds clearly predicted such phenomena.

Berthelot and Ilosvay[2] prepared the double salts $2KCl.SrCl_2$ and $2NaCl.$-

[1] W. D. Harkins and H. M. Paine, *J. Am. Chem. Soc.*, **38**, 2709 (1916).

[2] *Ann. chim.*, [5] **29**, 318 (1883).

$SrCl_2$, or $(SrCl_4)K_2$ and $(SrCl_4)Na_2$; and numerous other compounds of the same type have long been known. In fact, chemical literature abounds with references to such complexes, many stable and definitely characterized, and others too unstable for isolation under the conditions studied, but giving clear manifestations of their existence in aqueous solution.[1]

In the discussion of the mass law as applied to the ionization of electrolytes, most recent text-books of physical chemistry offer very little idea of the mechanism of the formation of the different ionic species represented. Mixed salt solutions, or even single salt solutions of the uni-univalent type, are undoubtedly very complex; but mass-law considerations are usually based on the simple assumption that the equilibrium corresponds more or less closely, in the case of potassium chloride, for example, to

$$KCl \rightleftarrows K^+ + Cl^-,$$

representing the ionization as a sort of splitting of the solute into parts, and, as Kendall[2] has said, "The solvent is relegated to the role of dead space." Ideas concerning the mechanism of the actual processes occurring between solvent and solute are not seriously considered in these texts.

Werner's conceptions lead to the same conclusions as thermodynamics in regard to the processes in aqueous solution;[3] in addition they also offer graphic pictures of mechanism, with which thermodynamics, caring only for the initial and final states, does not concern itself.

Further, it has been shown in this investigation that when amalgams of different concentrations are brought into equilibrium with individual salt mixtures, *e. g.*, with 0.2 *N* equivalent salt mixtures, it is necessary for these amalgams to adapt their free atomic concentrations so that in any case the free atomic fraction of potassium, and also that of strontium, is identical with the atomic fraction in all other cases. And in the case of each metal it has been shown that, provided the amalgam is sufficiently dilute, the free atomic concentration in the equilibrium amalgam is directly proportional to the hydrargyride concentration in the sense of the equation

$$Me + xHg = MeHg_x.$$

It has been found that, in the mixed amalgams of potassium and strontium, when in equilibrium with a mixed solution of fixed constitution, the free atom fraction of strontium rapidly decreases, while that of potassium correspondingly increases, in proportion to the total concentration of the amalgam. This shows that the degree of dissociation of the strontium hydrargyride is much less than that of the potassium hydrargyride, a fact which is in good agreement with the results of previous investigations.[4]

[1] Cf. Werner's, "*Neuere Anschauungen a. d. Gebiete d. anorg. Chemie*," 1913.

[2] *Loc. cit.*

[3] P. Pfeiffer, *Ber.*, **40**, 4036 (1907).

[4] Cf. G. McP. Smith, *Z. anorg. Chem.*, **58**, 381 (1908).

F. Summary.

1. The interaction equilibrium between mixed chloride solutions of potassium and strontium and dilute liquid amalgams has been studied, at various amalgam concentrations, in the following cases:

(*a*) Solutions of equivalent salt ratio, ranging in total concentration from 0.05 *N* to 3.0 *N*, at 25°, and with a total concentration ranging from 0.05 *N* to 0.8 *N*, at 40°.

(*b*) Solutions of varying salt ratio, at total concentrations ranging from 0.2 *N* to 0.8 *N*, at 25°.

2. The value of the "equilibrium expression" C_e increases directly with the concentration of the amalgam in all cases for amalgams containing up to about 0.3 milli-equivalent of metal per 10 g. of mercury.

3. With the assumption as a starting point that in solutions mixed in equivalent proportions, at a total concentration of 0.05 *N*, the simple K^+-ion and Sr^{++}-ion fractions are 0.6666 and 0.3333, ion-fraction calculations are offered for solutions containing the salts in equivalent proportions and also in varying proportions. The ion fractions are not directly proportional to the mol fractions of the salts.

4. The effect of temperature on the interaction equilibrium between 0.05 *N*, 0.1 *N*, 0.2 *N*, 0.4 *N*, and 0.8 *N* solutions and amalgams of varying concentration has been studied between 15° and 40°, and the heats of the different interactions have been calculated by means of the van't Hoff equation. This interaction heat increases gradually with decreasing total salt concentration.

5. The mass-action expression $[Me]/[MeHg_x] = K_{Me}$ has been shown to hold for potassium and strontium hydrargyrides in the presence of one another at total concentrations up to about 2 milli-equivalents per 100 g. of mercury.

6. The results of the investigation, in so far as the salt mixtures are concerned, have been shown to be in harmony with A. Werner's conceptions concerning the formation and dissociation of higher-order compounds.

BIOGRAPHY.

The writer of this thesis received his early education in the public schools of Denver, Colorado. He entered the University of Denver in 1909 and was graduated with the degree of Bachelor of Arts in 1913. He specialized in Chemistry throughout his course and acted as an Assistant in Chemistry under Professor W. D. Engle during the years 1911–1913. He returned to the University of Denver as an Instructor in Chemistry and received the degree of Master of Arts in 1914. During the academic years, 1914–1917, he held the position of Assistant in Chemistry in the University of Illinois and in 1917–1918 that of Fellow in Chemistry in the University of Illinois. During his four years at the University of Illinois, the writer has been engaged in graduate study in Analytical-Inorganic, Physical and Organic Chemistry and during the summers of 1915–1916–1917 he was employed as a Research Chemist on Smoke Investigations for the Garfield Plant of the American Smelting and Refining Company. He is a member of Phi Lambda Upsilon and Sigma Xi.